JOURNAL OF

The Electrochemical Society

VOLUME 95 NUMBER 2

February 1949

Published by

THE ELECTROCHEMICAL SOCIETY

Journal of The Electrochemical Society

Number 2 February 1949 Volume 95

Current Affairs

Editorial
The Unpredictable 25C
Meet Philadelphia 26C
Men and Ideas Across Houston Way 27C
[illegible] 34C
[illegible] 35C
Members of Other Organizations 35C
[illegible] 36C
[illegible] 37C
[illegible] 38C

Feature Section

The Federation of Electrochemical Societies
Invites the Young Graduate [illegible] 39
[illegible] Conference Reports 40

Technical Papers

[illegible] 23
[illegible] 33

EDITORIAL STAFF
H. H. Uhlig
Editor
Eleanor Reid
Assistant Editor

EDITORIAL BOARD
W. J. Alexander
C. L. Faust
H. J. Read
E. G. Reid
W. J. Reed
Chairman
J. M. Blalock
Paul T. Bruiller
N. C. Cahoon
C. L. Faust
H. C. Froelich
A. L. Hartlish
E. R. Saniger
Sherlock Swann, Jr.
Archie J. Weith

THE ELECTRODEPOSITION BEHAVIOR OF A SIMPLE ION[1]

L. B. ROGERS[2] AND A. F. STEHNEY[3]

Oak Ridge National Laboratory, Oak Ridge, Tennessee

ABSTRACT

The electrodeposition behavior of a trace on an inert electrode can be described by the unabridged form of the Nernst equation after it has been modified by the addition of a term to account for energy differences at the deposit-electrode interface. Both the original and the modified Nernst equations predict that, in dealing with amounts of depositable element insufficient to cover completely the inert electrode, the percentage of an ion deposited at any specific potential is independent of the amount of element present, but is dependent upon the area of the electrode and the volume of the solution.

INTRODUCTION

Successful electrolytic separations of some of the radioactive elements found in nature (Bi, Pb, Po) have been possible for many years (4). The method has, however, been applied to very few artificially-produced radioactive elements despite the fact that many elements can be electrodeposited easily.

The reluctance of investigators to exploit this method of separation appears to have been due to their concern as to whether or not the Nernst equation, or some comparable expression, could be used to describe the behavior of traces. Haissinsky (4) has discussed the results of many potentiometric and electrolytic studies in which the Nernst equation was tested with very dilute solutions, and he has found statements in support of both sides of the question. However, the conclusions of some of the authors are not valid because the authors overlooked the fact that two predictions can be made from the Nernst equation depending upon whether the usual "active" electrode, one whose entire surface is composed of the material being deposited, or a partially covered "inert" electrode is in equilibrium with the solution. The chief difficulty appears to be that some investigators, who concluded that the Nernst equation did not apply, tested the abbreviated form of the equation, which applies only to a covered electrode, in a situation where they were actually dealing with an incompletely covered inert electrode. This error has appeared quite frequently despite the fact that the work of Hevesy (7), in 1912, indicated that the complete Nernst equation should be used in such a situation. On the basis of Hevesy's results, Herzfeld (6) suggested that if the Nernst relation de-

[1] Manuscript received September 15, 1948. This paper prepared for delivery before the Philadelphia Meeting, May 4 to 7, 1949.

[2] Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Massachusetts.

[3] Present address: Department of Chemistry, University of Chicago, Chicago, Illinois.

fined the equilibrium potential of a completely covered electrode under a condition such that the rate of deposition equalled the rate of dissolution, the rate of dissolution for an incompletely covered electrode having fewer atoms of deposit per unit of surface area should be smaller. In order for an incompletely covered electrode to be in equilibrium with a particular concentration of ion, its potential would have to differ from that of a covered electrode in the same solution.

The present paper is an extension of Herzfeld's concept. It points out that the Nernst equation predicts that the position of the deposition curve, where one plots "percentage of element deposited" versus "potential," should be independent of the amount of reducible element involved providing: (a) the "inert" electrode is incompletely covered with deposit, and (b) all other experimental factors are held constant. Furthermore, the equation predicts that the deposition curves should shift with changes in electrode area, volume of solution, and size of the deposited atom (or aggregate). Any factor involving changes in the number of deposited atoms on the surface at the solution-electrode surface will also produce a shift. In conclusion, the paper points out that another term must be added to the Nernst equation to account for energy changes originating at the deposit-electrode interface.

DISCUSSION

Deposition of a single simple ionic species according to Nernst

The Nernst equation [using the Lewis and Randall (9) convention for signs] has been found to describe the potential on an inert electrode

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \tag{1}$$

for a reversible reaction involving only soluble ions where a_{ox} is the activity of the oxidant and a_{red} the activity of the reductant. One example is the reaction

$$Fe^{2+} \rightleftarrows Fe^{3+} + e \tag{2}$$

If one of the species is deposited, the electrode can no longer be considered "inert" but instead is termed "active." In the usual case where one is dealing with relatively large amounts of material, an inert electrode is almost instantaneously covered with deposit by the passage of current following which the electrode potential for a simple reaction such as

$$Ag \rightleftarrows Ag^+ + e \tag{3}$$

can be described adequately by an abbreviated form of the Nernst equation

$$E = E^0 - \frac{RT}{nF} \ln a_{ox} \tag{4}$$

in which the activity of the deposit is assumed to be constant and is defined as unity.

If only trace amounts of deposit are involved and the inert electrode is not completely covered by the deposit, the activity of the deposit should, according to Herzfeld (6), vary with the fraction of the surface covered.

By making an assumption, which will be discussed more fully in a later section, that the free energy required to deposit an atom is independent of the electrode material, one can write equation (1) in the form

$$E = E^0 - \frac{RT}{nF} \ln \frac{C_{ox} f_1}{f_r f_2} \tag{5}$$

where f_r is the fraction of the surface covered by the deposit and f_1 and f_2 are the activity coefficients of the ion and the deposited atom respectively. In an experiment, appropriate values can easily be determined for f_1 whereas f_2 is indeterminate, at least for the present, and will be considered to be unity.

Equation (5) can be extended by using the following terms:

A_a = cross-sectional area, in cm.^{2}, of an atom of deposit
A_e = area of the electrode in cm.^{2}
V = volume, in liters, of the solution in equilibrium with the electrode
C^0 = molar concentration of a solution of volume V which, if completely deposited on an electrode of area A_e, would be just sufficient to form a monolayer
C = initial molar concentration of reducible (or oxidizable) ions
C_{ox} = equilibrium concentration of reducible ion
$(C - C_{ox})\,V$ = total moles of atoms on the electrode surface at equilibrium
N_a = Avogadro's number
N^0 = total number of reducible ions and atoms involved
N_{ox} = number of reducible ions in solution at equilibrium
N_{red} = number of atoms deposited at equilibrium
x = fraction of element deposited at equilibrium
$E_{50\%}$ = potential at which $C_{ox} = \frac{C}{2}$ and therefore $N_{ox} = N_{red}$

The discussion can be simplified by making the following assumptions:

(a) The area of the electrode is equal to the area of a monolayer of deposit which, to a first approximation, can be expressed as a mathematical product of the cross-sectional area of the deposited atom and the number of such atoms.

(b) A second layer of atoms is not formed until the surface of the electrode has been completely covered with a monolayer.

(c) A simple reaction is considered which involves only electron transfer without any change in complexity in going from ion to deposit, i.e.

$$(M_y) \rightleftarrows (M_y)^{n+} + ne$$

It is then possible to express the activity of a deposit on an incompletely covered electrode of "inert" material as

$$a_{red} = f_r f_2 = \frac{N_{red} A_a f_2}{A_e} = \frac{(C - C_{ox}) V N_a A_a f_2}{A_e}. \tag{6}$$

Whenever $(C - C_{ox})$ is equal to (or greater than) C^0, a monolayer (or more) can be formed thereby producing a deposit with an activity which, by definition, has the limiting maximum value of unity.

$$(a_{red})_{max} = \frac{C^0 V N_a A_a f_2}{A_e} = 1 \tag{7}$$

In these terms, the potential of a completely covered electrode dipping into a solution of unit activity would be E^0 expressed as

$$E^0 = \frac{RT}{nF} \ln \frac{A_e}{C^0 V N_a A_a f_2} \tag{8}$$

For the general case, the equilibrium potential of an incompletely covered electrode dipping into a solution having the concentration C_{ox} can be obtained by substituting equation (6) into equation (5).

$$E = E^0 - \frac{RT}{nF} \ln \frac{A_e}{V N_a A_a} - \frac{RT}{nF} \ln \frac{f_1}{f_2} - \frac{RT}{nF} \ln \frac{C_{ox}}{C - C_{ox}} \tag{9}$$

Recalling that $E_{50\%}$ was defined as the potential at which $N_{ox} = N_{red}$ and $C_{ox} = C - C_{ox}$, one can write

$$E = E_{50\%} - \frac{RT}{nF} \ln \frac{C_{ox}}{C - C_{ox}} \tag{10}$$

or

$$E = E_{50\%} - \frac{RT}{nF} \ln \frac{1 - x}{x} \tag{11}$$

where

$$E_{50\%} = E^0 - \frac{RT}{nF} \ln \frac{A_e f_1}{V N_a A_a f_2}. \tag{12}$$

Equation (12) is equivalent to

$$E_{50\%} = E^0 - \frac{RT}{nF} \ln \frac{C^0 f_1}{f_2} \tag{13}$$

Because equation (11) has a constant point of inflection at $E_{50\%}$, the potential at which a specific percentage of a trace will deposit on an incompletely covered electrode should, in a series of similar electrolyses, be independent of the initial concentration of reducible ion.

Since equation (11) applies only when the inert electrode surface is incompletely covered, equation (11) will describe the complete deposition curve only when the total amount of depositable element is smaller than C^0. For amounts larger than C^0, equation (11) will describe the deposition only until an amount equal to C^0 has deposited following which, because equation (9) reduces to equation (4), the deposition will be described by equation (4).

If the deposition takes place from a solution having the reducible element in the form of a complex ion, it is necessary to take into consideration the activity of the complex-forming ion or molecule if it differs from unity. An ion or molecule, g, having b groups coordinated with the reducible ion introduces an additional term

$$E = E_{50\%} - \frac{RT}{nF} \ln \frac{1 - x}{x} - \frac{bRT}{nF} \ln C_g f_g \tag{14}$$

where C_g is the molar concentration and f_g the activity coefficient of the complexing ion. The complex-forming ion will usually be present in large excess, and will, therefore, be the chief factor influencing the activity coefficient of the reducible ion.

If precipitation occurs as a result of anodic oxidation the following set of equations can be written:

$$E = E^0 - \frac{RT}{nF} \ln \frac{VN_a A_a}{A_e} - \frac{RT}{nF} \ln \frac{f_2}{f_1} - \frac{RT}{nF} \ln \frac{C - C_{red}}{C_{red}} \tag{15}$$

$$E = E_{50\%} - \frac{RT}{nF} \frac{C - C_{red}}{C_{red}} \tag{16}$$

and

$$E = E_{50\%} - \frac{RT}{nF} \ln \frac{x}{1 - x} \tag{17}$$

where C_{red} is the concentration of the oxidizable ion. If the oxidation involves a complex ion, a term must be introduced in the same way that it was done for a reduction except that its sign should be reversed.

An additional consideration is introduced by the fact that anodic reactions often deposit an oxide rather than the free element. In such cases, A_a will be the area of the oxide molecule and the scope of $E_{50\%}$ must be expanded to include a consideration of the activity of the oxonium ion. A complete equation can be developed for every reaction in a way similar to that for the following example:

$$Pb^{++} + 6H_2O \rightleftarrows PbO_2 + 4H_3O^+ + 2e \tag{18}$$

and

$$E = E_{50\%} - \frac{RT}{nF} (a_{H_3O^+})^4 - \frac{RT}{nF} \ln \frac{C - C_{red}}{C_{red}}. \tag{19}$$

At a constant pH,

$$E = E'_{50\%} - \frac{RT}{nF} \ln \frac{x}{1 - x} \tag{20}$$

where

$$E'_{50\%} = E_{50\%} - \frac{RT}{nF} \ln (a_{H_3O^+})^4. \tag{21}$$

Any factor which affects the assumption that the rate of dissolution of the deposit is proportional to the number of deposited atoms will produce change in the observed activity of the deposit and, consequently, a change in the value of $E_{50\%}$. One mechanism by which atoms can be removed from the surface of the electrode is by diffusion of the deposit into the body of the electrode material. Another mechanism involves the formation of aggregates or multilayers of deposit. In both cases, the observed activity of the deposit would be lowered and the overall behavior of the trace changed to more "noble." In actual practice it might be possible to ignore these considerations providing that short periods of electrolysis and amounts of deposit covering only a small fraction of the electrode surface were involved.

Interfacial considerations not included in the Nernst equation

All of the preceding discussion has been based upon the assumption that the energy required to deposit an element is independent of the surface upon which it is deposited. That is to say, it has been assumed that the energy involved in depositing a silver atom on a silver surface is the same as for a silver atom on a platinum ("inert") surface. The literature contains much evidence which, if not in direct support of this postulate, at least indicates that the deposition behavior of a trace element on a number of different "inert" elements is the same (1, 2). However, a number of exceptions have been reported by the same and other authors (4).

In order to have an equation which will describe all of the experimental results, it is necessary to introduce a term which will take into consideration any difference in free energy, E_a, between the deposition of an atom on a surface of similar atoms and on a surface of dissimilar atoms. It is quite likely that deposition onto a dissimilar surface might liberate additional free energy due to alloy formation and possibly sorption. Equation (9) and subsequent equations must therefore be expanded to

$$E_{50\%} = E^0 - E_a - \frac{RT}{nF} \ln \frac{A_e f_1}{V N_a A_a f_3} \tag{22}$$

where f_3 represents the activity coefficient of the deposited atom whose standard state, where f_3 is unity, is the most stable alloy form. If E_a is positive, the trace should behave more nobly than predicted from the Nernst equation (Eq. 9). If E_a is negative, one should observe a shift of the deposition curve in the opposite direction thereby leading one to conclude erroneously that the deposition was obeying equation (4). A negative value for E_a might result in deposition curves which would drift, with longer periods of electrolysis, toward more negative potentials (for a reduction) due to the greater stability of aggregates of deposit compared to a random distribution of atoms over the "inert" surface.

It appears that the deposition curve of a trace might undergo a shift to more positive potentials if the surface of the "inert" electrode were dissolving. In order to gain the same net rate of deposition as that observed for an insoluble (or more slowly soluble) electrode, a more positive potential would be required (for a reduction) in order to decrease the rate of dissolution of the surface and to increase the rate of deposition of the trace. Experiments with silver tracer (3) have indicated that such a process may be an important consideration, but in the face of such a conclusion, one has evidence that chemical replacement is a satisfactory method for the separation of a trace element (12, 13). Reconciliation of these two observations appears to be possible, but no attempt will be made to do it here.

In reconsidering as a whole the question of electrodeposition of a trace by reduction, it is important to note that both the original and the modified forms of the Nernst equation predict that the $E_{50\%}$ should be independent of the amount of element undergoing reaction providing the amount is insufficient to form a monolayer. For that reason, one must reconsider the conclusions from experiments similar to those recently reported by Heal (5). Heal concluded that the Nernst equation did *not* describe the deposition of a trace because: (a) his deposition curves did not shift with dilution, and (b) his curves agreed within experimental error with those

obtained by another investigator who worked with more concentrated solutions of the same element. Actually, the question which might be raised is why his data for the deposition potential agreed with those of the other investigator if changes in area of the electrode and volume of the solution are important considerations. This agreement could be explained by assuming that the investigators accidently used A_e/V ratios which were the same within the limits of experimental error.

Complex electrode reactions

As long as the assumption is valid that the complexity of the ion and of the atom is the same, equations (11), (17), and (20) will apply to aggregates of any complexity from simple ions to colloids, providing the aggregates have a uniform charge-to-size ratio. An interesting special case is encountered if n is smaller than y because the overall result is the deposition of an atom of M by a fraction of an electron. As examples of this behavior, one might imagine the deposition of aggregates such as $Mo_6Cl_8^{4+}$ and $Ta_6Cl_{12}^{++}$ (11). It is quite possible that the deposition of polonium, which puzzled Haissinsky (4) because it required only $\frac{1}{3}$ of an electron per atom, falls into this class. In the case of polonium, however, one cannot make a definite statement that a polymeric ion is the source of the anomaly, even though polonium polymers are known, because the conclusions were based upon data obtained by a rate-of-deposition technique (8, 10) in which the mechanism of the reaction may play an important role.

If the complexity of the ion differs from that of the deposit, the $E_{50\%}$ and the subsequent dependent terms are no longer independent of the amount of reducible element. This conclusion can be reached easily by examining values of the logarithmic term (and its derivatives) containing x.

CONCLUSIONS

Although the information in most of the papers in the literature is too scanty to allow a definite statement to be made, it appears that some investigators have erroneously reported that the Nernst equation did not describe the deposition of traces because they tested the abridged form rather than the complete equation. Nevertheless, it appears that the equation may be inadequate because it does not include a term to describe energy differences in the deposit-electrode interface. This energy factor is undoubtedly an important one not only in theoretical studies of trace deposition, but also in commercial electroplating where one is interested in determining how firmly an electrodeposit will adhere to the underlying material.

ACKNOWLEDGMENTS

The authors are indebted to Dr. Sidney Ross and Dr. K. A. Kraus for many helpful discussions and criticisms. It was Dr. Kraus who suggested that consideration be given to the effect of difference in the free energy of deposition on various surfaces.

This work was performed under Atomic Energy Commission contract No. W-35-058 eng. 71 with the Monsanto Chemical Company and contract No. 7405 eng. 26 with Carbide and Carbon Chemical Corporation.

Any discussion of this paper will appear in the discussion section of Volume 95 of the TRANSACTIONS of the Society.

REFERENCES

1. A. Coche, *Compt. rend.*, **225**, 936 (1947).
2. A. Coche and M. Haissinsky, *Compt. rend.*, **222**, 1284 (1946).
3. J. C. Griess, Jr., and L. B. Rogers, Unpublished studies.
4. M. Haissinsky, "Electrochemie des substances radioactives et des solutions extrement dilues," Hermann et cie, Paris (1946). See also: M. Haissinsky, *J. Chim. Phys.*, **43**, 21 (1946).
5. H. G. Heal, Report MC-33 to National Research Council of Canada, December 18, 1943.
6. K. F. Herzfeld, *Physik. Z.*, **13**, 29 (1913).
7. G. Hevesy, *Physik. Z.*, **12**, 715 (1912).
8. F. Joliet, *J. Chim. Phys.*, **27**, 119 (1930).
9. G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York (1923).
10. F. Paneth and G. Hevesy, *Wien. Ber.*, **122**, 1037, 1049 (1913); **123**, 1619 (1914).
11. L. Pauling, *Chem. Eng. News*, **25**, 2970 (1947).
12. E. Rutherford, J. Chadwick, and C. D. Ellis, "Radiations from Radioactive Substances," p. 554, Cambridge University Press, London (1930).
13. G. T. Seaborg, C. D. Coryell, et al., Plutonium Project Record, CL-440, p. 53, July, 1942.

THE ELECTRODEPOSITION BEHAVIOR OF TRACES OF SILVER[1]

L. B. ROGERS,[2] D. P. KRAUSE,[3] J. C. GRIESS, JR., AND D. B. EHRLINGER[4]

Oak Ridge National Laboratory, Oak Ridge, Tennessee

ABSTRACT

By means of radioactivity, the extent of silver deposition on platinum cathodes was determined at various potentials under conditions closely approaching equilibrium. For any specific solution having a concentration of silver of 10^{-5} M or greater, the resulting curve agreed well with the polarographic curve. For concentrations equal to or smaller than 10^{-7} M, the amount of silver was insufficient to cover the electrode and the resulting deposition curves often shifted to a potential several tenths of a volt more "noble" than that predicted by the Nernst equation. The shift, which may be the result of alloy formation, was influenced greatly by the "inert" electrode material.

Changes in the electrode area and in the volume of solution were found to shift the position of the deposition curve in accordance with predictions based upon the Nernst equation. Complexing agents decreased and sometimes eliminated the shift toward noble behavior whereas, in one case, a higher concentration of acid produced a larger shift toward "nobility."

INTRODUCTION

The question of whether or not the electrodeposition behavior of traces can be predicted by the Nernst equation is a classical one. Haissinsky (1), in reviewing the subject, pointed out that there are many contradictory conclusions in the literature, some of which undoubtedly stem from the fact that some investigators have tested an abridged equation rather than the complete Nernst expression. It appears that the complete Nernst expression plus an additional term to account for differences in free energy arising at the deposit-electrode interface from the use of different "inert" electrode materials may be correct (2). It was suggested that the deposition behavior of traces should be affected by changes in area of the electrode and volume of the solution, but not by changes only in the total amount of trace element undergoing reaction. The experiments described in the present paper were designed to test these predictions and to provide information concerning the types and the magnitudes of errors encountered in the various procedures.

[1] Manuscript received October 4, 1948. This paper prepared for delivery before the Philadelphia Meeting, May 4 to 7, 1948.

[2] Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

[3] Present address: Argonne National Laboratory, Chicago, Illinois.

[4] Present address: Northwestern University School of Law, Chicago, Illinois.

Silver was selected for this study because of its favorable chemical and radiochemical properties. The electrode reactions of silver are one-electron transfers which are readily reversible. The relatively "noble" potentials at which many of the reactions take place help to minimize dissolution losses in handling the electrodeposits. Furthermore, although silver is an uncommon impurity in reagents, it can, if present, be reduced to a very low concentration by electrolysis. Finally, silver has a radioactive isotope (Ag^{111}), having a 7.5 day half-life and a 1.0 Mev. β^- particle, which can be produced with an adequately high specific activity to allow accurate measurement of the relative amount of silver in a very dilute solution.

All of the data were calculated on the basis of formal potentials (3) which were first obtained polarographically and then checked by electrodeposition using 10^{-5} M solutions. Factors such as activity coefficients, junction potentials, and concentration of the complexing agent were held constant throughout the series of experiments involving a particular background solution.

EXPERIMENTAL DETAILS

Apparatus

All of the equipment employed in this study was the same as that reported previously (4): a modified Sargent Model XX polarograph, a constant-voltage regulator capable of control to ±3 mv., a Beckman pH meter fitted with a special electrode having a small correction for sodium ion, special electrolytic cells enabling the deposition to be confined to a fixed area on one side of a platinum foil, and standard equipment for β^- particle counting consisting of a thin mica end-window Geiger-Muller tube, an aluminum-lined lead shield, and a scaling circuit.

Reagents and solutions

Reagent grade chemicals were used throughout this investigation. Distilled water was used in most of the experiments except those involving traces of silver where triply-distilled water was employed. The triply-distilled water was prepared from the laboratory supply of distilled water by distillation in an all-glass apparatus, first from alkaline permanganate and then from phosphoric acid. Starting in each case with two liters of water, the fraction between 25 and 75 per cent was collected. The final distillate did not give a positive test for silver when examined with a procedure sensitive to 0.05 μg./ml. (5).

Whenever possible, a solution of each reagent was freed from natural silver by electrolysis before the tracer was added. Such a procedure was deemed advisable even for the palladium (Baker and Co.) which sometimes contained spectrographically-detectable amounts of silver of the order of 50 p.p.m. (6). The procedure for the removal of silver impurity was the same as that used to recover the silver tracer following the neutron-bombardment of palladium. In addition, two steps were necessary in order to recover the purified palladium metal prior to activation. The entire procedure is outlined below.

A 50 mg. portion of palladium metal was dissolved in a mixture of nitric and sulfuric acids. After cooling, the solution was diluted to about

100 ml., neutralized by adding pellets of sodium hydroxide slowly, and then made 1.0 M in sodium hydroxide and 0.10 M in sodium cyanide. This solution was electrolyzed for three hours using a platinum gauze electrode maintained at −1.2 v. vs. the saturated calomel electrode (S.C.E.). After removing the electrode, the electrolysis was repeated using a second clean electrode. Then, palladium cyanide was precipitated by adding sulfuric acid, and washed with triply-distilled water. The final step of the purification consisted of dissolving the palladium cyanide in sulfuric acid followed by the precipitation of palladium metal by formaldehyde. The product was always spectrographically-free from silver, i.e. less than about 10 p.p.m. (6).

Ag^{111} tracer having a high specific activity was prepared by bombarding natural palladium with neutrons,

$$Pd^{110}\ (n, \gamma)\ Pd^{111} \xrightarrow[26\ m.]{\beta^-} Ag^{111} \xrightarrow[7.5\ d.]{\beta^-} Cd^{111}\ (stable),$$

dissolution of the palladium, and recovery of the silver by electrolysis with a platinum electrode (4). By carrying out three electrolyses in series, the amount of palladium accompanying the silver was reduced to a very small value (calculated to be less than 1% of the amount of silver). However, small amounts of platinum undoubtedly dissolved from the cathode along with the silver when the latter was stripped from the electrode into the desired background solution. Calculations indicated that if one could neglect the amount of silver introduced as an impurity, the resulting tracer solutions were about 1×10^{-9} M in silver.

Procedures

Polarograms for silver in various background electrolytes were recorded automatically using a solid electrode, usually platinum, and an outside saturated calomel electrode (7, 8).

Electrolyses were carried out in essentially the same way that has been described previously (4). A glass tube, having both ends open, was clamped onto a platinum foil to define a circle having a plane area of about 5 $cm.^2$ The capacity of a cell was about 35 ml. but 25.0 ml. was used for most of the experimental work. The solution was stirred at 300 r.p.m. using a glass rod having a single small paddle. All glass surfaces, including those of the stirrer and the agar bridges, were given a fresh coat of ceresine wax before each experiment in order to minimize losses from sorption. Platinum electrodes were usually sufficiently free from silver (and radioactivity) to be used again after a preliminary cleaning in boiling nitric acid followed by immersion in a solution of sodium cyanide for several hours.

In the interest of minimizing losses of deposited silver while the electrode was being washed, the following variation from the original procedure (4) was introduced: After the stirring had been stopped and most of the active solution removed by suction, the potential of the cathode was made about 0.5 v. more negative. The amount of material plated from an unstirred solution was negligible, but the additional voltage appeared to help in holding the deposit while it was being washed with the recommended (4) nitrate or perchlorate solution. The activity on the cathode was then dis-

solved in a solution of cyanide by electrolysis for a few minutes at a positive potential to strip the radio-silver from the electrode. The activity in a sample of the "strip" solution was then determined.

Some studies were made by depositing the trace completely and then adjusting the potential to the desired value. This proved to be a useful method for finding the approximate (sometimes exact) location of a deposition curve because a number of potentials could be examined consecutively in a short time. In general, a stripping procedure allowed one to approach more closely to an equilibrium value in a short interval of time than a deposition procedure did. Sampling (50 or 100 μl.) of the supernatant between each setting of potential resulted in negligible losses of solution.

Standard radiochemical techniques were used for the estimation of activity. All counts were made under conditions such that back-scattering, self-scattering, and geometry were held constant. Coincidence corrections

TABLE I. *Comparison of polarographic and deposition curves for silver in five media*

Background electrolyte	$E_{1/2}$ vs. S.C.E. 10^{-3} M	$E_{50\%}$ for 10^{-5}M vs. S.C.E.		$E_{50\%}$ for 10^{-3}M vs. S.C.E.	
		Predicted from $E_{1/2}$	Experimental value	Predicted from $E_{1/2}$	Experimental value
0.1 M KNO_3 pH = 4.0	+0.32	+0.20	+0.21	+0.08	+0.48
0.1 M $NaClO_4$ 1.0 M $HClO_4$	+0.32	+0.20	—*	+0.08	+0.60
0.1 M NH_3	−0.02	−0.14	−0.10	−0.26	−0.05
0.1 M NaCN	−0.84	−0.96	−0.88	−1.08	−0.95
0.1 M NaCN 1.0 M NaOH	−0.79	−0.91	−0.89	−1.03	−0.99

*No experimental value obtained.

were made when necessary. All measurements were relative rather than absolute.

RESULTS

Change in $E_{50\%}$ with concentration of silver

The change in $E_{50\%}$, the potential at which half of the silver is precipitated on a silver electrode, can be predicted from the equation

$$E = E^0_f + \frac{RT}{nF} \ln C \qquad (1)$$

where E^0_f is the formal potential for the reaction in question, C is the molar concentration of the reducible ion, and the polarographic convention is used for signs. Providing overvoltage from factors other than concentration polarization can be neglected; $E_{50\%}$ for an electrodeposition should agree with the polarographic halfwave potential ($E_{1/2}$).

Typical evidence of such agreement for solutions having initial concentrations of silver equal to or greater than 10^{-5} M is shown in Table I.

It was generally possible to reproduce the values for $E_{1/2}$ or $E_{50\%}$ within ± 0.01 v. Deposition results for a solution of 0.1 M sodium perchlorate at pH 4 are not shown because they agreed with those for nitrate. It was found that the disagreement between $E_{50\%}$ and $E_{1/2}$ for a solution containing 0.1 M cyanide and 1.0 M hydroxide could be eliminated by changing manually the potential on the polarographic slidewire and waiting 15 minutes or more at each potential before reading the current. The disagreement, therefore, was attributed to overvoltage in the automatically recorded polarographic curve.

Calculations showed that 25 ml. of a 5×10^{-7} M solution of silver would be sufficient to form a monolayer on a 5 cm.^{2} area. It was not surprising, therefore, that 10^{-7} M and more dilute solutions deviated from values calculated from equation (1).

However, this behavior is in accordance with the predictions of an equation based upon an early suggestion of Herzfeld (9) that the activity of the deposit might vary with the fraction of the surface covered with deposit. This can be stated as (2):

$$E = E_f^0 + E_a + \frac{RT}{nF} \ln \frac{A_e f_1}{V N_a A_a f_3} + \frac{RT}{nF} \ln \frac{1 - x}{x} \qquad (2)$$

where E^0_f = formal potential for a covered electrode
E_a = potential associated with free energy of alloy formation (at the deposit-electrode interface)
x = fraction of the initial amount of element deposited at potential E
V = volume of solution
A_e = electrode area
A_a = area of a deposited atom
N_a = Avogadro's number
f_1 and f_3 = activity coefficients of the ion and deposited atom respectively

By combining the first three terms one obtains $E_{50\%}$ for a particular set of experimental conditions:

$$E_{50\%} = E_f^0 + E_a + \frac{RT}{nF} \ln \frac{A_e f_1}{V N_a A_a f_3} \qquad (3)$$

It is apparent from equations (2) and (3) that one would expect the position of the deposition curves or trace amounts to be independent of initial concentration of reducible element when the electrode area and the ionic strength and volume of solution are held constant.

The examples shown in Fig. 1 illustrate the types of curves that were found. One very important aspect of a curve for trace amounts was its comparatively poor reproducibility, which usually corresponded to nearly $\pm$ 30 mv., despite the fact that the regulators controlled the potential to $\pm$ 3 mv. or better. Several factors, particularly differences in areas of the electrodes, contributed errors which will be discussed later.

As one might have expected, 10^{-6} M solutions gave a curve having certain characteristics of both "macro" and trace curves. The results in Fig. 2 indicate that, except for one curve, the $E_{50\%}$ value fell close to ± 0.14 v., the value predicted from equation (1). However, in common with curves for trace amounts, there was appreciable plating at potentials sev-

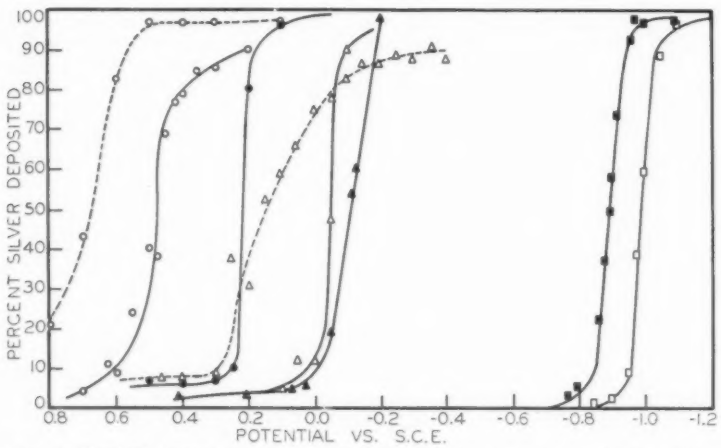


FIG. 1. Typical deposition and stripping curves for silver in various media. ○ "Trace" silver in 0.1 KNO_3 pH 4.0, ● 10^{-5}M silver in 0.1 M KNO_3 pH 4.0, △ "Trace" silver in 0.1 M NH_3, ▲ 10^{-5}M silver in 0.1 M NH_3, □ "Trace" silver in 0.1 M NaCN + 1.0 M NaOH, ■ 10^{-5}M silver in 0.1 NaCN + 1.0 M NaOH. The dotted lines indicate the corresponding stripping curves.

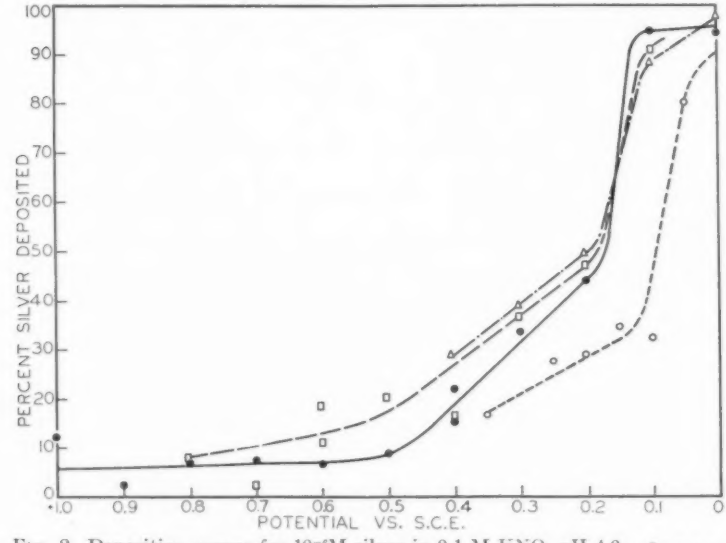


FIG. 2. Deposition curves for 10^{-6}M silver in 0.1 M KNO_3 pH 4.0. ○- - - - - - Run No. 1, ● ———— Run No. 2, □- - - - - -Run No. 3, △- - - · - - - · Run No. 4.

eral tenths of a volt more positive than the $E_{50\%}$. Furthermore, the amount of scatter in the values for percentage of silver deposited at any specific

potential more positive than $E_{50\%}$ was characteristic of that found in experiments with trace amounts.

Two important conclusions were made during the course of this study. The first was that the behavior of an ion in contact with an incompletely covered electrode might be quite different from its "macro" behavior. Instead of changing with the initial concentration of solution in accordance with equation (1), the $E_{50\%}$ for traces was constant within the rather wide limits of error. This was demonstrated by agreement between curves for 10^{-7} M and "trace" solutions. It is true that one can argue that the amount of impurity remaining in reagents was the limiting factor which remained constant, but it appears highly probable that such was not the case in view of extraordinary precautions which were taken to reduce the silver content of all reagents.

The second conclusion drawn from the deposition curves for traces was that E_a could cause a sizeable shift in the deposition curve. If E_a were zero, the curve for trace amounts would be displaced from E^0_f by an amount $+\frac{RT}{nF} \ln \frac{A_e f_1}{V N_a A_a f_3}$. Table I shows that such a displacement was found for cyanide solution. On the other hand, substantial shifts of the deposition curve to positive potentials were found in ammonia, nitrate, and perchlorate solutions.

The fact that E_a was not independent of the medium can be explained if one assumes that the anion substantially affects the rate of dissolution of the "inert" electrode. Qualitatively, there are many pieces of evidence to support this assumption: (a) At comparable potentials, the silver can be removed from an electrode much faster with a cyanide solution than with a nitrate solution. Complete removal of activity is also easier to effect. (b) In working with trace amounts, stripping curves agree very well with deposition curves for cyanide solution whereas for nitrate, perchlorate, and ammonia solutions the stripping curves are displaced about +0.2 v. from the respective deposition curves.

Since the value for E_a should be the same for each solution only if the rate of dissolution of the "inert" electrode is the same, the maximum value for E_a should be found for the solution for which the rate of dissolution of the "inert" electrode is slowest. One would expect to find the maximum value for E_a in nitrate or perchlorate medium since these anions would form the least stable complexes (if any) with the platinum. On the other hand, it is also conceivable that the rate of dissolution of an "inert" electrode in certain solutions might be so fast that the deposition curve for a trace would be displaced to a value more negative than that calculated from equation (2) on the assumption that E_a were zero.

The observed effect of perchloric acid in increasing the nobility of silver on platinum can be interpreted on the foregoing basis. However, it is also possible that a mechanism involving changes in the amount of platinum oxide (or hydrogen) on the surface of the electrode might be involved. More evidence is needed before a definite statement can be made.

Change in $E_{50\%}$ with volume of solution

Equation (3) predicts that if two solutions initially contain the same total number of reducible ions and are electrolyzed under otherwise identical conditions, the solution having the smaller volume will have the larger

number of ions removed by deposition. The procedure which follows was designed to test that prediction.

A 5.00 ml. portion of 0.1 M potassium nitrate solution at pH 4.0 to which silver tracer had been added was electrolyzed at a potential sufficient to precipitate most, if not all, of the silver. The activity of the solution was determined both before and after electrolysis by counting an aliquot of the supernatant. After the potential had been changed to strip the activity from the electrode the supernatant was sampled again. The analysis of the first supernatant together with the difference between the two was assumed to represent the percentages actually involved in the deposition equilibrium. The difference in activity between the second sample of the supernatant and the amount initially present before electrolysis represented the loss due to sorption and to diffusion into the salt bridges.

TABLE II. *Effect of volume on $E_{50\%}$ for a trace of silver in 0.1 M KNO_3 at pH 4.0*

Potential vs. S.C.E.	Activity in solution / Activity on cathode			Deviation from calculated value
	5 ml.	25 ml.	Calc. for 25 ml.	
	%	%	%	mv.
+0.470	3/97	31/69	13/87	29
+0.470	5/95	24/76	20/80	6
+0.500	20/80	54/46	53/47	1
+0.500	41/59	74/26	74/26	0
Average				9

The volume of the solution was then increased to 25 ml. by the addition of 20 ml. of 0.1 M KNO_3 (pH 4.0) and the silver redeposited. Again the activity of the supernatant was determined before and after stripping the deposit from the electrode. The position of the $E_{50\%}$ for the silver in each volume was calculated by substituting the equilibrium values into equation (2) to determine $E_{50\%}$. The deposition curves were assumed to be symmetrical in making the calculation.

The data shown in Table II substantiate very satisfactorily the prediction of equation (3). The fact that the data were so good is probably the result of having only one electrode of fairly constant area involved in each comparison. The agreement obtained in these experiments (plus the fact that all of the changes were somewhat greater than predicted) is evidence that the wide limits of error found in the deposition curves where several electrodes were involved was largely the result of differences in the electrode area.

Change in $E_{50\%}$ with A_c

Indirect evidence has already been presented to support the idea that the

electrode area is an important factor affecting the extent of deposition of a trace. It was evident that any attempt to evaluate this factor quantitatively would be limited by the reproducibility of the curves. This reproducibility was first determined by calculating the $E_{50\%}$ value for several points on a curve using the equation

$$E = E_{50\%} + \frac{RT}{nF} \ln \frac{(1 - x)}{x} \qquad (4)$$

When this was done for a number of curves, the values were regularly found to spread over 50–60 mv. An independent check was then made by determining one experimental point 15 times using a different electrode each time. After being boiled in nitric acid for 30 minutes, electrodes 1 through 8 were allowed to stand in a warm solution of cyanide for an hour before being used whereas electrodes 9 through 15 were not removed from the cyanide for 64 hours. From the averages of the percentage plated on the two groups of cathodes, one can calculate that the average increase in area resulting from the prolonged treatment with cyanide was 2.7 fold. This change might have been somewhat greater if new platinum electrodes had been used for the first group of experiments instead of electrodes which had already been used many times. However, an overall average of the data in Table III represents the extremes encountered in the present study in selecting an electrode at random and cleaning it. It is important to note that the maximum spread of 54 mv. confirms the other results.

TABLE III. *Study of the duplicability of the per cent silver deposited from 5 ml. of 0.1 M KNO_3 (pH 4.0) on 5 cm.² platinum at +0.500 v. vs. S.C.E.*

Cathode no.	Activity			Material balance
	Cathode	Supernatant	Bridges	
	%	%	%	%
1	87	7	4	98
2	99	2	4	105
3	91	5	5	101
4	55	36	5	96
5	74	18	6	98
6	94	4	2	100
7	64	26	20*	110*
8	80	14	7	101
9	98	2	2	102
10	90	2	6	98
11	91	2	4	97
12	94	1	2	97
13	94	4	1	99
14	92	2	2	96
15	88	4	4	96
Average	86 ± 10	9	4	99

* Probably in error; omitted from average.

Ave. 1–8: 81 ± 12% = 23 mv. variation in $E_{50\%}$.

Ave. 9–15: 94 ± 3% = 15 mv. variation in $E_{50\%}$.

Ave. 1–15: 86 ± 10% = ± 27 mv. variation in $E_{50\%}$.

To study the change of $E_{50\%}$ with area, convenience favored the choice of a smaller rather than a larger electrode for comparison with the standard 5.0 cm.^{2} electrode. It was found that a wire of about 0.14 cm.^{2} plane area would reach essentially an equilibrium value in 15 hours time when the volume of solution was 5.0 ml. Because of the limits of error in the overall procedure, the resulting factor of 35 could barely produce a significant result, and even then only if a sufficiently large number of determinations were made to allow statistical reasoning to be used. For that reason, it is interesting to observe that although the results presented in Table IV are too few to allow conclusions of quantitative nature to be made, they do indicate a trend in the proper direction, i.e., less plating on the smaller electrode.

TABLE IV. *Effect of electrode area on $E_{50\%}$ for a trace of silver in 5 ml. of 0.1 M KNO_3 at pH 4.0*

Potential vs. S.C.E.	Activity in solution / Activity on cathode			Deviation from calculated value
	5.0 cm.^{2}	0.14 m.^{2}	Calc. for 0.14 cm.^{2}	
	%	%	%	*mv.*
+0.470	5 / 95	81 / 19	64 / 36	23
+0.470	5 / 95	66 / 34	64 / 36	2
+0.500	14 / 86	66 / 34	89 / 11	38
+0.500	14 / 86	92 / 8	85 / 15	19
Average				20

The procedure was as follows: The amount plated onto a 5.0 cm.^{2} electrode was determined using the procedure described in the preceeding section. In getting data for the smaller electrode a sheet of waxed paper was substituted for the 5.0 cm.^{2} electrode in the regular cell. The micro electrode was prepared by sealing a platinum wire above it into a glass tube, immersing the wire and about three inches of glass tubing into melted wax, and then scraping the wax from a measured portion of the wire with a razor blade. The exposed portion of wire was carefully cleaned in the usual way with nitric acid followed by cyanide. A study of the rate of plating from 5.0 ml. showed that in 15 hours one reached greater than 97 per cent of the equilibrium value, so a 15 hour electrolysis was made before determining the distribution of tracer.

Influence of the electrode material on $E_{50\%}$

All of the experiments that have been described above were carried out with platinum electrodes. There is much evidence in the literature (1, 10, 11, 12) that variations arising from differences in electrode materials

are often very slight, but the results given below for tantalum, gold, rhodium, palladium, and tungsten indicate that such agreement may be exceptional.

The study consisted of three parts: (a) a polarographic study of the deposition of "macro" amounts of silver on the various elements, (b) a rapid non-equilibrium determination of a deposition curve for a trace of silver,

TABLE V. *Effect of various electrode materials on the $E_{1/2}$ of a 10^{-3} M silver solution in 0.1 M $NaClO_4$ at pH 4.0*

Electrode material	$E_{1/2}$ vs. S.C.E.
Gold	+0.35 v.
Palladium	+0.32 v.
Platinum	+0.31 v.
Rhodium	+0.30 v.
Tantalum	+0.26 v.*
Tungsten	+0.28 v.

* Two smaller waves were found with halfwave potentials at +0.13 v. and −0.49 v.

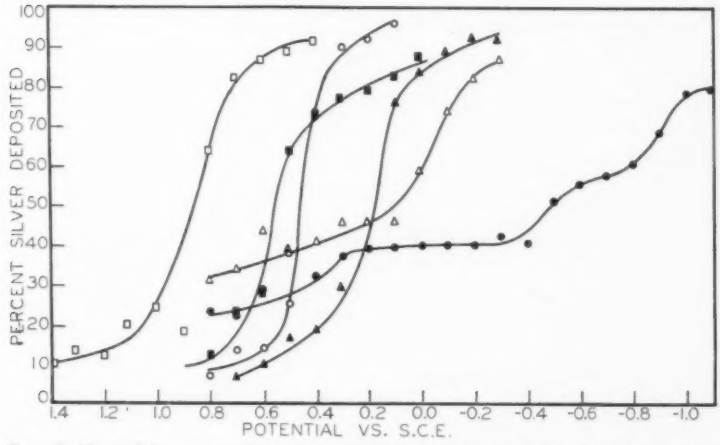


FIG. 3. Deposition curves for a "trace" of silver in 0.1 M KNO_3 (pH 4.0) on various electrode materials. □ Gold, ■ Platinum, ▲ Tungsten, △ Rhodium, ○ Palladium, ● Tantalum.

and (c) a rapid non-equilibrium determination of the reversibility of the deposition. It was hoped that by running platinum along with the other metals, a rough control would be available by which to judge how far the last two types of curves for each element deviated from equilibrium values. Points were taken after 30 minutes at a particular potential.

The polarographic halfwave potentials for a millimolar solution of silver in 0.1 M perchlorate at pH 4.0 are listed in Table V. Although the values are rather close to one another, one should note that there is a spread of nearly 0.1 v. in the halfwave potential despite the fact that it is usually

possible to duplicate halfwave potentials for a platinum electrode within ±0.01 v. (7). It seems reasonable to conclude, therefore, that the differences in polarographic behavior are real.

It was interesting to find that the deposition curves for tracer silver followed essentially the same pattern as the polarographic curves (Fig. 3). The $E_{50\%}$ for silver on gold was more noble while those for tungsten and tantalum were less noble than the value for platinum.

The respective stripping curves (Fig. 4) produced very marked differences: (a) The wave for tungsten was poor and stripping was incomplete; (b) Tantalum, even at +2.6 v., had stripped only a few per cent more than it had at +1.2 v.; (c) While the platinum stripping wave shifted about

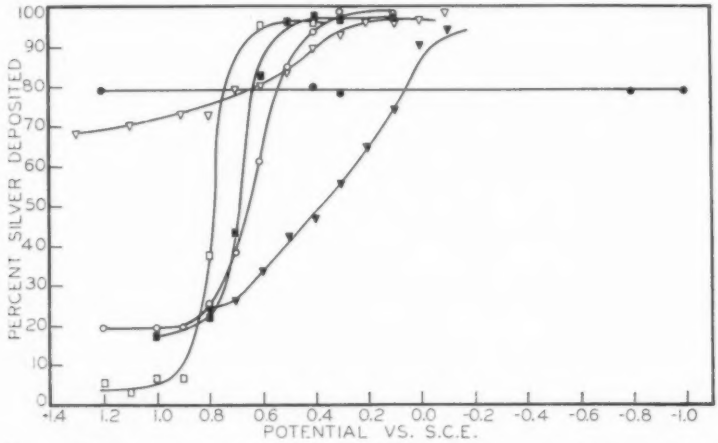


FIG. 4. Stripping curves for a "trace" of silver on various electrode materials in 0.1 M KNO_3 pH 4.0. □ Gold, ■ Platinum, △ Tungsten, ▲ Rhodium, ○ Palladium, ● Tantalum.

+0.2 v. from the deposition wave, the dissolution wave for gold was shifted −0.06 v.

Spectrographic analyses indicated that before any depositions had been made rhodium, tungsten, and tantalum were spectrographically free from silver while platinum, palladium and gold had trace amounts present. However, the observed differences in behavior cannot reasonably be attributed to variations in the amount of silver in the materials.

Miscellaneous studies

Before carrying out the experiments described up to this point, the relative importance of each experimental factor was evaluated as carefully as possible. For example, a determination of the time required for complete (98%) plating was carried out every time a change was made in electrode area, volume of solution, or electrode material. Each rate-of-plating curve was established with five or more points.

Reproducibility tests were made for all plating and stripping curves.

At the same time extensive studies of sorption losses were also made. Ceresine wax was found to be the most suitable substance for covering the glass surfaces. It was found, too, that in working with nitrate and perchlorate solutions the use of a waxed paper gasket was much better than one of scotch tape. The fact that absorption losses decreased with increasing stability of the silver complex suggests that better recoveries and improved analytical separations should result from the use of more stable complexing agents.

The question of whether or not the curves represented equilibrium data is primarily a matter of definition. It was sometimes difficult to remove the activity entirely from an electrode, an experience that most investigators have encountered. Furthermore, in determining the rates of plating and stripping two very distinct rates were noted in each curve. For example, in plating silver from 25 ml. of a solution onto a 5.0 cm.^{2} electrode, the rate of plating was rapid for the first five hours. During the following 24 hours, the activity in the supernatant dropped about 25 per cent. An analogous study of stripping rates showed an abrupt change in rate between 15 and 30 minutes after electrolysis began, and, after 24 hours, the activity of the supernatant had increased about 35 per cent.

There is no doubt that silver diffused into platinum to form a solid solution. A true equilibrium value would require a homogeneous solid solution to be in equilibrium with the aqueous solution and, by using data obtained after 5 hours of plating, one is dealing with a constantly changing system. However, since the rate of diffusion in the solid is slow compared to the rate of plating, it should be possible to arrive at a first approximation to an equilibrium value by electrolyzing only until the rate of plating changed. The value thus obtained is in equilibrium only with respect to a thin layer of the "inert" electrode (13). Attainment of equilibrium with a homogeneous solid solution was impractical in these studies where it was desirable to use .004 in. (.01 mm.) foil because of its sturdiness.

As yet, insufficient information is available to allow a reliable calculation of E_a to be made. It has been pointed out that factors other than E_a, especially the rate of dissolution of the electrode, will influence the position of a deposition curve for a trace. It is apparent that before investigations can be undertaken to study changes in E_a (or f_3) with changes in the fraction of a surface covered by an "active" (in the thermodynamic sense) deposit, a more exact knowledge of electrode area and rates of dissolution is necessary.

It is also apparent that except for the solutions containing 1 M acid or base, the absence of a buffer resulted in appreciable changes in pH during an electrolysis. Changes as great as 4 or 5 units were quite common. For example, 0.1 M potassium nitrate at pH 4.0 was usually about pH 10.2 after a five hour electrolysis. Although such changes were undesirable, they were quite uniform at all potentials on a particular curve. For that reason the absence of a buffer was not felt to be serious, and its absence reduced the complexity of the solution.

CONCLUSIONS

Evidence has been presented to show that the volume of solution and the electrode area affect the position of a deposition curve for a trace concentration of silver. The position of the curve is independent of the initial

concentration of the trace. This behavior can be predicted from the Nernst equation providing one assumes that the thermodynamic activity of the deposit varies with the fraction of the "inert" electrode surface covered by the deposit. For that reason, the investigators who assumed that the activity of the deposit would always have a value of unity (1, 12, 14) were in error in concluding from their data that a Nernst-type expression did not describe the deposition behavior of traces. However, it does appear that the Nernst equation is inadequate for other reasons, namely, that the free energy of alloy formation and the rate of dissolution of the "inert" electrode must be considered.

ACKNOWLEDGMENTS

The authors are very much indebted to C. B. Pickle and R. W. Lamphere of the Instrument Department for the design of the voltage regulators which made this study possible. The authors wish to thank C. Feldman and M. Murray for making the numerous spectrographic analyses required for this study.

This work was performed under Atomic Energy Commission contracts No. W-35-058 eng. 71 with Monsanto Chemical Company and No. W-7405 eng. 26 with the Carbide and Carbon Chemical Corporation.

Any discussion of this paper will appear in the discussion section of Volume 95 of the TRANSACTIONS of the Society.

REFERENCES

1. M. HAISSINSKY, *J. Chim. Phys.*, **43**, 21 (1946).
2. L. B. ROGERS AND A. F. STEHNEY, *J. Electrochem. Soc.*, **95**, 25 (1949).
3. E. H. SWIFT, "A System of Chemical Analysis," p. 50, Prentice-Hall, Inc., New York (1940).
4. J. C. GRIESS AND L. B. ROGERS, *J. Electrochem. Soc.*, In press.
5. I. M. KOLTHOFF AND R. S. LIVINGSTON, *Ind. Eng. Chem., Anal. Ed.*, **7**, 209 (1935).
6. C. FELDMAN, Private communication.
7. L. B. ROGERS, H. H. MILLER, R. B. GOODRICH, AND A. F. STEHNEY, *Anal. Chem.*, In Press.
8. E. M. SKOBETS AND S. A. KACHEROVA, *Zavodskaya Lab.*, **13**, 133 (1947).
9. K. HERZFELD, *Physik. Z.*, **14**, 29 (1913).
10. A. COCHE, *Compt. rend.*, **225**, 936 (1947).
11. A. COCHE AND M. HAISSINSKY, *Compt. rend.*, **222**, 1284 (1946).
12. C. H. HAENNY AND P. MIVALEZ, *Helv. chim. Acta.*, **31**, 633 (1948).
13. B. V. ROLLINS, *J. Am. Chem. Soc.*, **62**, 86 (1940). See also: G. V. Hevesy and Biltz, *Z. physik. Chem.*, B, **3**, 271 (1929); through reference 12.
14. H. G. HEAL, Report MC-33 to National Research Council of Canada, December, 1943.

THE ELECTROCHEMICAL PROCESS FOR THE PRODUCTION OF FLUOROCARBONS[1]

J. H. SIMONS AND COWORKERS

Fluorine Laboratories, The Pennsylvania State College, State College, Pennsylvania

A direct electrochemical method for the preparation of fluorocarbons in which elementary fluorine is neither produced nor employed is described in the five parts of this article. All previous methods for producing these substances involved the use of elementary fluorine either through direct reaction with carbon or carbonaceous substances or in the preparation of intermediate metal fluorides such as CoF_3 or AgF_2.

This process consists of passing an electric current through a simple one-compartment cell containing an electrically-conducting hydrogen fluoride solution and an organic compound or compounds. In some cases the organic compound forms an electrically-conducting solution but in others, as for example hydrocarbons, addition of a third substance to impart conductivity enables the process to be used. The products are isolated from the cell gases or are drained from the bottom of the cell depending on their boiling points.

I. The Generalized Procedure and Its Use with Nitrogen Compounds

J. H. Simons

ABSTRACT

A description is herein given of the general method by which fluorocarbons and some of their derivatives are obtained from hydrogen fluoride, an organic compound, and an electric current.

The cells used are made of any material resistant to hydrogen fluoride; the cathodes are usually iron and the anodes nickel. The cells are usually operated at potentials of five to six volts. At these potentials fluorine is not generated, but at much higher potentials it is with resulting explosions and extensive decomposition of the organic material.

The principal fluorocarbon product contains the same number of carbon atoms as the hydrocarbon radical of the organic compound.

The process is illustrated in the employment of pyridine as the source material and other nitrogen-containing examples. The peculiar behavior of mercuric cyanide in the cells is described.

INTRODUCTION

The desirability of other methods of producing fluorocarbons became immediately evident upon the discovery of the original preparation,

[1] Manuscript received September 7, 1948. This paper prepared for delivery before the Philadelphia Meeting, May 4 to 7, 1949.

separation, and identification of liquid fluorocarbons from the mercury catalyzed reaction of fluorine and carbon reported by Simons and Block (1). The original method has been repeated on a much larger scale with the identification of more compounds by Simons and Pearlson (2).

Although fluorocarbons in a mixture of a large number of compounds are produced in this manner, each compound is in relatively small percentage of the total and separation difficulties are encountered. It would be desirable to find a process that would be more specific for the preparation of particular compounds and it would be particularly advantageous if this process did not require the use of elementary fluorine. As soon as the original work had shown the desirable properties of the fluorocarbons, experiments were immediately initiated on other methods for attaining these desired ends. A direct electrochemical method was discovered in these laboratories which did this, and a paper describing some of the early work was accepted for publication by the *Journal of the American Chemical Society* in 1941, but was withdrawn for security reasons. It follows in Part II of this paper in essentially its original form.

HISTORICAL

Other methods of producing fluorocarbons have also been found. Fredenhagen and Cadenbach (3) controlled reactions between elementary fluorine and liquid hydrocarbons by the beneficial geometry of fine mesh copper screening. No fluorocarbons were produced but complex products containing a small percentage of fluorine were obtained. Miller, Calfee, and Bigelow (4) employed the same idea for the partial replacement of the chlorine of hexachloroethane with fluorine in the vapor phase. Employing the same technique Young, Fukuhara, and Bigelow (5) fluorinated ethane and obtained some C_2F_6. It was not until Fukuhara and Bigelow (6) tried benzene that liquid fluorocarbons were produced. Cady, Grosse, Barber, Burger, and Sheldon (7) improved this technique by silver plating the copper gauze to provide a catalytic surface in addition to the advantages of geometry provided previously and made the production of specific fluorocarbons more feasible by this method. Ruff, and Ruff and Ascher (8), showed the preparation of cobaltic fluoride, and Fisher and Jaenckner (9) used it in the synthesis of sulfur fluorides. Ruff and Keim (10) used it in the replacement of chlorine with fluorine in carbon tetrachloride. Cobaltous fluoride is converted to cobaltic fluoride by elementary fluorine and the reaction reduces this back to the cobaltous state from which it is reoxidized by fluorine. Fowler, Burford, Hamilton, Sweet, Weber, Kasper, and Litant (11) employed this technique with hydrocarbons and prepared large quantities of fluorocarbons. Good yields of specific products are produced by this process. Another interesting method of producing fluorocarbons has been reported by Park, Benning, Downing, Laucius, and McHarness (12). From chloroform, CF_2ClH is made using the Swarts reaction. A thermal decomposition of this material yields, in addition to C_2F_4, small amounts of the cyclic fluorocarbons C_3F_6, C_4F_8, and compounds of the formula $H(CF_2)_xCl$. The compound with $X = 14$ has been separated. These compounds can be chlorinated to replace the hydrogen atom, and then by exhaustive and vigorous fluorination, the chlorine replaced with fluorine. Straight chain and certain cyclic fluorocarbons can be obtained by this path.

Another interesting method of producing fluorocarbons is reported by Miller, Ehrenfeld, Phelan, Prober, and Reed (13). Elementary fluorine reacts with a completely halogenated olefin in the liquid phase at low temperature to cause coupling in addition to removal of unsaturation by addition of fluorine. An interesting example is the addition of fluorine to $CFCl{=}CFCl$. In addition to other products, $CF_2Cl{-}CFCl{-}CFCl{-}CF_2Cl$ is obtained. Dechlorination yielded $CF_2{=}CF{-}CF{=}CF_2$. On further liquid phase fluorination of this diolefin, fluorocarbons such as C_8F_{18} and $C_{12}F_{26}$ were obtained.

GENERALIZED TECHNIQUE AND EQUIPMENT

The electrochemical process consists of passing an electric current through a simple one compartment cell containing organic chemical compound or compounds, and an electrically conducting solution containing hydrogen fluoride. Many organic compounds, particularly those containing oxygen or nitrogen, have relatively high solubility in liquid hydrogen fluoride and form an electrically conducting solution. Others, such as hydrocarbons, are not very soluble and do not form conducting solutions, but fortunately the addition of some material which imparts conductivity enables the process to be used even with hydrocarbon starting materials.

The cells can be constructed of any material, such as iron or copper, not readily attacked by hydrogen fluoride. The electrodes can be in a compact pack with alternating cathodes and anodes. The cell body can serve as part of the cathode. The anodes are usually nickel, but other metals show promise. Cathodes can be nickel, iron, copper, and many other conductors. Hydrogen is generated and gaseous or readily volatilized products escape with the hydrogen. Liquid products form a layer in the bottom of the cell and are drained off. Voltages between 5 and 8 are useful but between 5 and 6 are preferred. Sometimes even lower voltages are possible. Current density in the order of 0.02 ampere per sq. cm. can be employed.

The cells normally operate without the generation of elementary fluorine. At the potentials employed, no fluorine is produced. If the potential is raised so that the element is a product, extensive corrosion of the electrodes occurs, some fluorine escapes and can be detected in the exit gas, minor or even major explosions occur, and undesirable decomposition of the organic materials results. Satisfactory yields of fluorocarbons under these conditions are not obtained.

Various size cells have been used as this process developed. The first ones were only slightly larger than a test tube. Much of the experimental work was done with cells 3 inches in diameter and 12 inches long which carried 3 to 4 amperes. For larger quantities of materials, cells were used which carried 50 to 200 amperes. At present a cell carrying 2000 amperes is employed. It has been convenient for laboratory reasons to operate the cells in ice baths at or near 0°C. because of the loss by vaporization of the hydrogen fluoride; but by increasing the pressure, higher temperatures have been used. This loss of hydrogen fluoride can be reduced by other means, such as reducing its vapor pressure with solutes, low temperature stripping condensers on the exit line, etc.

A great variety of organic compounds has been used. Examples of some of these are reported in the following parts of this paper. Carboxylic acids

are generally useful, as are alcohols, ethers, amines, etc. Even hydrocarbons can be used to yield high percentages of the corresponding fluorocarbon, such as octforane from octane. From the carboxylic acids, in addition to saturated fluorocarbons corresponding to the hydrocarbon radical, a significant amount of hydrogen-containing product is obtained, such as CF_3H from acetic acid, C_2F_5H from propionic acid, C_3F_7H and $C_3F_6H_2$ from butyric acid, etc. From some of the oxygen-containing substances OF_2 (particularly if water is present) is a product, and ways of both minimizing it and destroying it have been found. NF_3 is a product from

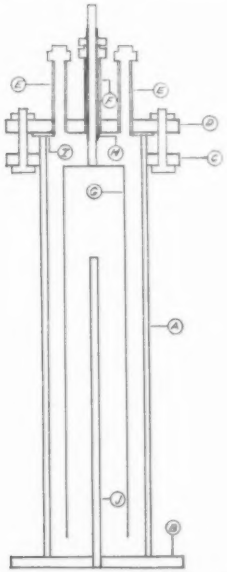


FIG. 1. Fluorocarbon producing cell (laboratory size). A. Cell body of 3 in. iron pipe, B. base of $\frac{1}{4}$ in. iron plate silver soldered, C. flange brazed to cell body, D. top iron plate, E. inlet and outlet tubes of $\frac{1}{4}$ in. iron pipe, F. copper tubing anode support $\frac{1}{2}$ in. O.D., G. anode, H. Saran tubing insulation, I. gasket, J. center cathode.

certain nitrogen-containing starting materials. CO_2 and even CO are found in some cases but the former is more prevalent.

In some cases resinous material is formed in the cell. In most cases this is soluble in the electrolytic solution and does not interfere with operation. Fluorine content up to 50 or 60 per cent has been found in these resins. In other cases no residual materials are found even after extended use of the cell. In general, there is little or no corrosion of the electrodes.

There is generally the greatest amount of product in the range of the number of carbon atoms in the organic radical of the starting material. In many cases products are obtained containing a larger number of carbon atoms per molecule than the starting materials, and there are frequently products containing less. Ethers give good yields of products in which the

number of carbon atoms is equal to the total number of carbon atoms per molecule of the ether. Products containing the number of carbon atoms of the hydrocarbon radical are also found.

EXPERIMENTAL

The cell used in the following experiments is shown in Fig. 1. It was made of a length of 3-inch iron pipe, 12 to 15 inches long.

Pyridine.—The cell was placed in a tube of ice and 700 grams of hydrogen fluoride were added. Current was passed through the cell until fluorine was generated. This was done to dry the liquid. Then 120 grams of redistilled pyridine were slowly added. The voltage remained relatively steady with an average of 5.7 and the average current was 4.0 amperes. In 76 hours 15.2 faradays were passed.

In gaseous products from the cell passed through a sodium fluoride tube to remove hydrogen fluoride, then into a trap kept in a solid carbon dioxide bath, and finally into a gas holder. From the gas holder the gas was dried and passed through a trap kept in liquid air. The gaseous products were found in the two traps. The liquid air trap contained a material boiling about −124°C. that had a molecular weight determined by gas density of 71–73. This material is nearly pure NF_3 and its total amount was 32 grams. Next, 168 liters of hydrogen were measured. In the solid carbon dioxide cooled trap were found 130 grams of material which boiled above room temperature. On distillation through an efficient laboratory column, 110 grams of it boiled 27–28°, had a determined molecular weight of 288, and showed 79 per cent fluorine by analysis. This material is pentforane, C_5F_{12}. The remaining 20 grams boiled progressively from 28° to above 50°.

The cell was examined after the termination of the experiment. It was found clean and without evidence of corrosion. There was some material other than hydrogen fluoride remaining. A considerable portion of this was unreacted pyridine but about 8 grams of 2-fluoropyridine were also found.

In a much larger scale experiment using pyridine as raw material, 1 kg. of NF_3 and 5 kg. of pentforane C_5F_{12} were recovered.

2-Fluoropyridine was also used as starting material with results not greatly different.

Quinoline was also used as starting material. The initial charge was 100 g. but an undetermined amount remained at the end of the experiment. Just as in the case of pyridine, nitrogen trifluoride was produced. Thirty-nine grams of fluorocarbons were obtained, of which 22.2 grams boiled 117–117.5°, had a determined molecular weight of 446, and had an analysis; F, 75.6 per cent; C, 23.1 per cent; H, 0.0 per cent (C_9F_{18}; mol. wt., 450; F, 76%; C, 24%).

Acetonitrile.—In an experiment using a technique similar to the one reported above, with the exception that the product was collected directly in a liquid air cooled trap, 20 faradays gave 201 grams of fluorocarbon products from a cell charge containing 205 grams of CH_3CN.

This experiment was unsatisfactory in that the cell developed a leak and transfer of the contents had to be made to a new cell. Although one third of the product was CF_4, small amounts of both CF_3CN and C_2F_5H were found. The CF_3CN occurred in a fraction boiling at −61°C. It reacted

with KOH solution with the evolution of ammonia. The dried salt was crystallized from absolute ethanol and by analysis found 36.1 per cent F (CF_3CO_2K, 37.5%). The hydroethforane C_2F_5H occurred in a fraction boiling $-47°$ to $-44°$ with a determined molecular weight of 119–124. Corrosion to the cell body and electrodes occurred in this experiment and inorganic salts were found in the cell after the conclusion of the experiment. The experiment is significant in showing that derivatives of fluorocarbons as well as the fluorocarbons themselves are produced by this process.

Mercuric cyanide.—The properties of mercuric cyanide in liquid hydrogen fluoride are both unusual and of some interest. As most soluble cyanides react with liquid hydrogen fluoride to liberate HCN, which is not soluble, and as HgF_2 is but slightly soluble in hydrogen fluoride, it is surprising that mercuric cyanide is both soluble in hydrogen fluoride and forms a conducting solution. A still more surprising fact, however, is that, at low voltages, this solution passes a direct electric current without the production of gaseous products and with the mercuric cyanide subsequently recovered from the solution.

In the same cell as used for the pyridine experiment, 60 grams of mercuric cyanide were added to 400 grams of hydrogen fluoride previously dried electrically. Five to 5.4 volts allowed 2.7 to 2.8 amperes to flow and this continued for the passage of 8.7 faradays. Two hundred cc. of gas were evolved at the start of the passage of current and none subsequently. There were recovered from the cell contents 55 grams of mercuric cyanide.

In order to increase the voltage, the anode area was reduced and the experiment repeated at higher potentials. A potential of 12 volts showed the production of fluorine but at the potential used, 7.4–7.8, no fluorine was produced: 4.4 faradays were passed; 11.8 liters of hydrogen and 12 grams of impure methforane CF_4 were obtained. The cell residue was mostly mercuric cyanide plus 12 grams of mercury.

ACKNOWLEDGMENT

The experimental work reported in Part I was done with the help of a project sponsored by the Minnesota Mining and Manufacturing Company.

REFERENCES

1. J. H. Simons and L. P. Block, *J. Am. Chem. Soc.*, **59**, 1407 (1937); **61**, 2962 (1939).
2. J. H. Simons and W. H. Pearlson, Work in preparation.
3. K. Fredenhagen and G. Cadenbach, *Ber.*, **67**, 928–35 (1934).
4. W. T. Miller, J. D. Calfee and L. A. Bigelow, *J. Am. Chem. Soc.*, **59**, 198 (1937).
5. De W. S. Young, N. Fukuhara and L. A. Bigelow, *ibid.*, **62**, 1171 (1940).
6. N. Fukuhara and L. A. Bigelow, *ibid.*, **63**, 2792 (1941).
7. G. H. Cady, A. V. Grosse, E. J. Barber, L. L. Burger and Z. D. Sheldon, *Ind. Eng. Chem.*, **39**, 290 (1947).
8. O. Ruff, *Z. Angewandte Chem.*, **41**, 738 (1928).
   O. Ruff and E. Ascher, *Z. anorg. allgem. Chem.*, **183**, 197 (1929).
9. J. Fisher and W. Jaenchner, *Z. Angewandte Chem.*, **42**, 810 (1929).
10. O. Ruff and R. Keim, *Z. anorg. allgem. Chem.*, **201**, 245 (1931).
11. R. D. Fowler, W. B. Burford, III, J. M. Hamilton, Jr., R. G. Sweet, C. E. Weber, J. S. Kasper, and I. Litant, *Ind. Eng. Chem.*, **39**, 292 (1947).
12. J. D. Park, A. R. Benning, F. B. Downing, J. F. Laucius, and R. C. McHarness, *ibid.*, **39**, 354 (1947).
13. W. T. Miller, Jr., R. L. Ehrenfeld, J. M. Phelan, M. Prober, and S. J. Reed, *ibid.*, **39**, 401 (1947).

II. The Electrolysis of Solutions of Organic Substances in Liquid Hydrogen Fluoride[2]

J. H. Simons, H. T. Francis, and J. A. Hogg

ABSTRACT

This paper describes the first experiments on the electrolysis of solutions of organic substances in liquid hydrogen fluoride.

The electrolysis of carboxylic acids and alcohol solutions in liquid hydrogen fluoride was found to yield fluorocarbons and hydrogen-containing fluorocarbons ranging from carbon tetrafluoride and fluoroform to materials boiling well above 100°C.

The products of the electrolysis of solutions of carboxylic acids in hydrogen fluoride would be expected to be different from those of electrolysis in water because of the known differences in the ions (1). In hydrogen fluoride the ions are $CH_3CO_2H_2^+$ and F^- while in water the ions are $CH_3CO_2^-$ and H^+. The products formed can be accounted for on the basis of the reactions of these ions at the electrodes and by the change in acid strength as fluorination proceeds. Alcohols and ketones also become positive ions in hydrogen fluoride and the electrolysis of their solutions may be similar to those of acetic acid.

INTRODUCTION

This investigation was undertaken to study the electrolysis of solutions of organic chemical substances in liquid hydrogen fluoride.

EXPERIMENTAL

The electrolysis cell was made of a cylindrical copper vessel to which was attached two outlet tubes on the side near the top. One of these was connected to a manometer. A nickel anode entered from the top of the vessel and was insulated either by means of a rubber stopper or by an annular seal of wax. The evolved gases were passed through either sodium fluoride or a solution of sodium hydroxide to remove hydrogen fluoride and then were collected over water in carboys.

Acetic acid.—A solution of one mol in 115 grams of hydrogen fluoride was electrolyzed at 0° until 4.5 faradays of electricity had passed. The average potential was 12 volts and current 5.2 amperes. In the evolved gases there was, in addition to carbon dioxide and hydrogen, a mixture of carbon tetrafluoride and fluoroform in a ratio of about one to two. The yield of fluorinated products based on the current consumption was about 50 per cent. No fluorinated acetic acids were found in the examination of the cell residue.

Acetyl chloride reacts with hydrogen fluoride to form hydrogen chloride and acetyl fluoride. This material was found to have a high electrical resistance in hydrogen fluoride so that sodium fluoride was added for electrolysis. After 4 faradays of electricity were passed at −80°C., a mixture of equal quantities of carbon tetrafluoride and fluoroform was obtained from the gaseous products. These represented a yield of fluorinated

[2] Part II of this paper was submitted to the Editor of the *Journal of The American Chemical Society*, April 3, 1941, but was withdrawn for security reasons after being accepted for publication. It is here reproduced essentially in its original form.

products of about 10 per cent based on the current passed. As trifluoroacetyl fluoride is a possible product and because of its low boiling point would be carried out of the cell with the escaping gases, the sodium hydroxide solution from the trap was examined for the salt of trifluoroacetic acid.

Acetone.—A solution of one mol in 130 grams of hydrogen fluoride was electrolyzed at 0° using a current of 5.4 amperes at 8 volts. About equal quantities of carbon tetrafluoride and fluoroform were found in the gaseous products in a yield based on current passed of approximately 25 per cent.

Trimethylacetic acid.—A solution of this acid was electrolyzed under similar conditions. Forty grams were dissolved in 200 grams of hydrogen fluoride. At a potential of 4 volts, 8 amperes of current passed until 120 liters of gas were collected. Of the material condensable in liquid air, about one third was carbon tetrafluoride and the rest probably OF_2. A small amount of tar was formed in the cell. The residual organic acid was found to give a negative test for fluorine.

Normal propyl alcohol (2 mols in 260 grams of hydrogen fluoride) was dissolved and the solution electrolyzed. The gaseous products were passed through an aqueous sodium hydroxide solution, water, concentrated sulfuric acid, and a receiver placed in liquid air. The condensate in the receiver was separated into three portions by simple distillation, from −128° to −75°, −75° to −25°, and −25° to +30°. The average molecular weights of these portions were respectively 119, 138, and 243. These products were concluded to be mixtures of fluorinated hydrocarbons with and without hydrogen in the molecules ranging from carbon tetrafluoride up to molecules containing more than three carbon atoms. Octafluoropropane has a molecular weight of 188 and boils at −38° (2). Since the gases were bubbled through sulfuric acid as well as water and a sodium hydroxide solution, alcohols, ethers, and similar compounds are probably absent. The residue from the cells, when freed from hydrogen fluoride and distilled, consisted of about 5 cc. of a mixture similar to that observed in the distillation of the gaseous products, but with a higher boiling range, 60° to 105°C. It was more dense than water and was immiscible with it.

Normal amyl alcohol gave products on electrolysis of its solution not greatly different than normal propyl alcohol except for somewhat higher boiling points. One hundred cubic centimeters of the alcohol was dissolved in 300 grams of hydrogen fluoride, and the solution electrolyzed with a current of 3.5 to 4 amperes at 8 to 9 volts for 100 hours, producing about 200 liters of gas. After the gas was scrubbed with both sodium hydroxide solution and sulfuric acid, about 20 cc. of liquid was condensed from it. About one fourth of this boiled up to room temperature but chiefly above the ice point. The remainder boiled between 30° and 135°. The remainder was divided into about four equal parts by simple distillation, the first of which boiled 30° to 45° and had a molecular weight of 196; the second, boiled 45° to 60° and had a molecular weight of 215; the third boiled 60° to 100° and had a molecular weight of 243; and the fourth boiled 100° to 135° and had a molecular weight of 340.

In the cell were found about 50 cc. of a thick brown liquid. It was insoluble in water but soluble in ether and in sulfuric acid. It apparently was polymerized organic material and resisted further investigation.

Acetic acid and also sodium acetate dissolved in molten $KF \cdot 3HF$ and electrolyzed at 75°C. gave a mixture of fluoroform and carbon tetrafluoride

in a ratio of about two to one, with a yield based upon current passed of about 40 per cent.

DISCUSSION

The products formed by the electrolysis of solutions of acetic acid in hydrogen fluoride would be expected to be different from those formed by the electrolysis of an aqueous solution because of the known difference in the ions (1). In hydrogen fluoride the ions are $CH_3CO_2H_2^+$ and F^-. The fluoride ion would move toward the anode and on discharging would react with organic material in solution, i.e., fluorinate the acetic acid. The $CH_3CO_2H_2^+$ ion would discharge hydrogen at the cathode. Fluorinated acetic acids might, therefore, be expected but we have been unable to detect them. However, as acetic acid is fluorinated and 1, 2, and 3 fluorine atoms introduced in place of the hydrogen atoms, the molecule becomes more acidic. If the di- and tri-fluoroacetic acids ionize as strong acids to produce di- and tri-fluoroacetate and hydrogen ions, a reasonable explanation of the products is available. An aqueous solution of acetic acid electrolyzes to produce ethane and methane, the relative amounts of which depend upon such factors as current density, the presence of other ions, etc. An aqueous solution of trifluoroacetic acid (3) produces some hexafluoroethane upon electrolysis. Thus, the trifluoroacetate ion would be expected to lose carbon dioxide upon discharging. The molecular fragment thus produced would immediately react. As fluoride ion is present in large excess and is also discharging at the same electrode, carbon tetrafluoride is the expected product. By similar reasoning fluoroform is the expected product from the discharge at the electrode of the difluoroacetate ion.

Acetone becomes a positive ion in liquid hydrogen fluoride, and the electrolysis of its solution may be similar to that of acetic acid. The partially fluorinated substances first formed undergo a break in a carbon–carbon bond either by electrolysis or by further fluorination. As acetyl fluoride is a poor conductor it is difficult to understand its behavior.

REFERENCES

1. J. H. Simons, *Chem. Reviews*, **8**, 213 (1931).
2. Simons and Block, *J. Am. Chem. Soc.*, **61**, 2692 (1939).
3. Swarts, *Bull. sci. acad. roy. Belg.*, **17**, 27 (1931).

III. From Hydrogen Fluoride-Soluble Organic Substances[3]

J. H. Simons and W. J. Harland

ABSTRACT

In Part II, the earlier work of Simons, Francis, and Hogg showed that fluorocarbons could be produced electrochemically. By the use of a bank of larger cells useful quantities of material were obtained, the nature of the fluorocarbon products was determined in greater detail, and the relative usefulness of various types of hydrogen fluoride-soluble organic compounds was estimated.

[3] Part III of this paper is based on a dissertation submitted February, 1944, by Walter J. Harland in partial fulfillment of the requirements of the degree of Doctor of Philosophy in the School of Chemistry and Physics, The Pennsylvania State College.

Proceeding from a carboxylic acid through an alcohol to an amine, the compounds become progressively more basic; at the same time, the spread of fluorocarbon products obtained becomes narrower and more closely concentrated in the region of the number of carbon atoms of the starting material. Used as starting materials in the process are n-amyl alcohol, valeric acid, and n-octyl amine.

INTRODUCTION

The preceding section of this paper showed the possibility of producing fluorocarbons by passing an electric current through a solution of an organic substance in hydrogen fluoride. This was particularly evident in the case of certain alcohols. Further work has now shown that considerable fluorocarbon products can be obtained in this way not only from alcohols but also from carboxylic acids, amines, etc. Examples of these are herein given.

EXPERIMENTAL

Apparatus and technique

A much larger cell than previously used was employed in order to obtain larger quantities of product. It was constructed of a three inch iron pipe fifteen inches long, closed at the bottom with a one-fourth inch iron plate (silver soldered), and at the top with an assembly carrying the anode held tight with a lead packing. The anode consisted of a sheet of $\frac{1}{32}$ inch nickel rolled into cylindrical form two inches in diameter and nine inches long and secured to a concentric one-fourth inch nickel rod which served both for electrical connection and physical support. It was insulated from the cell body by a seal of a mixture of two-thirds ceresin wax and one-third mineral oil. The cell body served as the cathode and had outlets for gaseous products consisting of one-fourth inch copper tubing silver soldered into the side wall of the iron pipe. It was charged through the same openings. Six of these cells were used at the same time in order to obtain significant samples of products. They were operated at a current density of about 0.012 amperes per sq. cm. This necessitated a voltage close to 5.5 for most substances.

In operation, these cells were charged, placed in a bath of ice and water, connections made, and current started. The gas escaping from the cell consisted chiefly of hydrogen contaminated with hydrogen fluoride evaporated from the electrolytic solution, and the other products formed as the result of the passage of the current. This gas was passed through a water scrubber to remove the hydrogen fluoride and then into 50 gallon steel drums arranged to serve as gas holders.

The temperature of the electrolytic solution is not a variable of major significance. These three inch iron pipe cells were not provided with means for determining the temperature of the solution in the cell. In operation this must be somewhat higher than the surrounding bath. Temperatures, therefore, were not determined for the solutions employed in the following reported experiments.

At the end of the experiment the products were obtained from the contents of the drums by passing the gas through a NaOH scrubber to remove CO_2 and then through traps immersed in liquid air. The cell contents were also examined.

n-Amyl alcohol.—Eight mols of alcohol was distributed to the six cells. Six hundred and seventy-five grams of hydrogen fluoride were charged to each cell initially and 300 grams added subsequently to make up for losses by evaporation and consumption by the process. The current was stopped after 185 hours and the use of 145 faradays. Twenty grams of CO_2 were obtained and 75 grams of gaseous products boiling up to the temperature of solid carbon dioxide mixture. This consisted of a mixture of CF_4, CF_3H, and C_2F_6, but it was not examined in detail. Two hundred and sixty grams of material boiling above −80° were fractionated (Table I).

Molecular weights were determined by means of a gas density balance previously described (1).

After residual hydrogen fluoride was allowed to evaporate from the cells, they were extracted with ether. The ether washings were extracted with sodium carbonate washed with water, dried, and the ether evaporated. Two hundred and sixty grams of a polymer were found which by analysis

TABLE I

Boiling range	% by wt. of total	Molecular weight
°C		
−38 to −16	6.2	197
−16 to −2	6.7	
−2 to +3	13.0	238
3 to 17	7.5	
24 to 25	12.9	
26 to 28	14.5	282
28 to 30	5.7	
35 to 45	10.5	
45 to 53	1.5	
53 to 70	3.7	340
70 to 75	2.1	
75 to 81	4.1	
81 to 86	3.6	
86 to 110	7.7	

had: C, 60.9 per cent; H, 7.8 per cent; F, 15.0 per cent. It was soluble in ether, acetone, acetic acid, methanol, and conc. H_2SO_4, but insoluble in water and 5 per cent NaOH. No etching was observed on the treatment with H_2SO_4 indicating tightly bound fluorine.

As alcohols polymerize in anhydrous hydrogen fluoride, the formation of polymer is not unexpected. In a check experiment, amyl alcohol could not be removed after six hours from its solution in hydrogen fluoride.

It is quite apparent that a distribution of fluorocarbons containing from one to eight atoms is produced with the greatest fraction being pentforane, C_5F_{12}, and the second fraction in amount being chiefly butforane, C_4F_{10}.

Valeric acid.—Each of five cells was charged with one mol of valeric acid and 675 grams of hydrogen fluoride. Current was passed at an average of 5.5 volts for 135 hours when the seals began to fail. The cells were removed from the circuit one by one to 166 hours. A total of 82 faradays was passed. Products obtained showed 30 grams of gaseous fluorocarbons boiling up to solid carbon dioxide temperature (CF_4, CF_3H, C_2F_6) and 377 grams of material boiling higher which was fractionated (Table II).

An examination of the cell contents showed no residue, polymer, or tars.

A mixture of fluorocarbons has been thus produced from a five carbon carboxylic acid ranging in number of carbon atoms from one to eight with a predominance of compounds containing four and five carbon atoms.

n-Octyl amine.—Each of four cells was charged with 0.42 mols of n-octyl amine and 500 grams of hydrogen fluoride. Current was passed at an average of 5.3 volts with each cell carrying 3 amperes. A total of 100 hours operation for two cells and 125 hours for the other two resulted in the passage of 53 faradays.

The gaseous fluorocarbon products boiling up to solid carbon dioxide temperature amounted to 12 grams. One hundred and ten grams of higher

TABLE II

Boiling range	% by wt. of total	Molecular weight
°C		
−50 to −35	7.8	
−30 to −20	4.3	187
−20 to −13	3.6	
−13 to −6	14.4	
−6 to 0	13.7	226
0 to 7	8.8	227
7 to 13	7.9	228
13 to 18	5.2	229
18 to 20	6.8	225
20 to 26	14.4	240
26 to 37	5.8	245
39 to 60	4.9	
60 to 100	2.4	

TABLE III

Boiling range	% by wt. of total	Molecular weight
°C		
35 to 51	4.4	
51 to 60	6.6	344
60 to 80	5.9	
80 to 83	15.9	422
83 to 101	15.4	
101.5 to 103.5	44.1	452
103.5 to 125+	17.7	

boiling liquids were distilled and no products obtained from −80° to +35° (Table III).

A residue was found in the cells which was divided into ether soluble and ether insoluble portions. The ether soluble portion was soluble in acetone, methanol, and acetic acid; insoluble in petroleum ether and conc. HCl; and decomposed in conc. H_2SO_4 and 20 per cent NaOH. It analyzed for no ionizable fluoride ion but 48.94–49.35 per cent total F. The ether insoluble portion contained iron, 35.6 per cent hydrolyzable fluorine by boiling with 25 per cent NaOH, and 50.7 per cent total F.

DISCUSSION

A comparison of the production of fluorocarbons by this direct electrochemical process shows several interesting facts. As we proceed from a

carboxylic acid through an alcohol to an amine, the compounds become progressively more basic. The spread of products becomes narrower and more closely concentrated in the region of the number of carbon atoms of the starting material. Both the alcohol and the amine showed disadvantages in the formation of polymeric substances, and the amine apparently formed products which reacted with the iron of the cell body.

REFERENCE

1. J. H. Simons, *Ind. Eng. Chem., An. Ed.*, **10**, 587 (1938).

IV. From Oxygen Containing Compounds

J. H. Simons, W. H. Pearlson, T. J. Brice, W. A. Wilson, and R. D. Dresdner

ABSTRACT

The electrochemical process for the production of fluorocarbons has been shown to function satisfactorily with a large range of oxygen containing organic compounds. With acids a spread of fluorocarbon products is obtained with the number of carbon atoms both less than and greater than the number of carbon atoms in the hydrocarbon radical of the acid. The most significant percentage, however, is in the fraction having this number of carbon atoms. A number of fluorocarbon hydrides have been isolated from the products. Alcohols and ethers also satisfactorily gave fluorocarbon products.

INTRODUCTION

In the preceding part of this paper there were indications that carboxylic acids and alcohols were preferred raw materials upon which to operate the electrochemical process for the preparation of fluorocarbons. We are herein reporting more extensive studies of a number of acids, alcohols, and ethers.

EXPERIMENTAL

Cells of three different sizes and design were employed.

Type A.—A cell similar to the one described in the preceding paper with two major changes. A $\frac{1}{2}$ inch iron post welded to the center of the bottom plate of the cell body doubled the capacity of the cell as use was made of both outside and inside surfaces of the cathode. The cell top was held by a gasket of Saran or Teflon and the anode rod was both held and insulated by slipping a piece of Saran tubing over it and tightening it in a $\frac{3}{8}$ inch compression fitting.

Type B.—A rectangular cell made of $\frac{1}{4}$ inch iron boiler plate approximately 6 in. x 15 in. x 27 in. high. Electrodes were made of sheet metal $\frac{1}{16}$ in. thick, 18 in. x 11.5 in. There were 8 anode plates of nickel and 7 cathode plates of iron. The cathodes were shorted to the cell body and the anode and cathode plates alternated in the electrode pack. The gasket for the cell cover and the insulation for the anode were made of Saran.

Type C.—This cell was circular in cross section. It consisted of a 6 inch iron pipe surrounded by a welded jacket of 8 inch pipe through which alcohol could be circulated as a cooling medium. The electrode pack consisted

of alternate sheets of $\frac{1}{16}$ inch nickel and iron approximately 4 inches wide and 9 inches long. Approximately 11 nickel and 10 iron sheets were used, the iron electrodes being shorted to the cell body. Saran gaskets and insulation were employed. The cell was provided with a condenser on the gas outlet through which cold alcohol from the refrigeration system could be circulated to remove excess hydrogen fluoride from the gas stream and return it to the cell. A series of electrical probes were provided which extended down from the cover plate. They were used to determine the height of the liquid in the cell. Pumping equipment was provided to charge the cell and replenish used raw material while in operation.

The exit gases from the cell were passed through dry sodium fluoride to remove hydrogen fluoride and then through a basic sodium thiosulfate solution to remove OF_2. From Cell A the gases were collected in gas holders over water, whereas for Cells B and C the gases passed counter current to a stream of aqueous ammonia in a tower to remove CO_2, then through bubblers of basic sodium sulfite containing catalytic amounts of KI to remove OF_2. Liquid air cooled traps collected about 90 per cent of the fluorocarbons. The hydrogen was burned in heated chambers of copper oxide and the residual fluorocarbons recovered from the exit gases in liquid air cooled traps. Means were provided for taking samples of the gas for analysis at various points of the purifying train.

Acetic acid.—Preliminary experiments reported in Part II of this paper indicated that both fluoroform and carbon tetrafluoride were obtained from acetic acid. To test this further and also obtain quantities of these substances for other experiments, the process was employed using acetic acid on a larger scale. Type C cells were used and a total of 11 kg. of purified methforane and 8 kg. of purified fluoroform were obtained. Current between 150 and 200 amperes passed through the cell at voltages between 6.0 and 7.5 with a current density of 0.04 amperes per sq. cm. Analyses of the gas stream after removal of hydrogen fluoride showed in volume percentage: H_2, 67; CO_2, 16; OF_2, 2.3; CF_4, 7.7; CF_3H, 1.3; and CFH_3 and higher boiling products, 0.3.

The common gases were analyzed in the usual manner, OF_2 was determined after absorption in a buffered KI solution by titrating the liberated iodine with thiosulfate solution, and CF_4, CF_3H, and CF_2H_2 were separated by distillation. A difficulty arose in the separation of CFH_3 as this apparently formed an azeotropic mixture of approximately equal molal amounts with CF_3H boiling at about $-78°$ at atmospheric pressure. A photochemical chlorination made $CFCl_3$ from CFH_3, whereas CF_3H was untouched.

In order to study the relative amounts of CF_3H and CF_4, both concentration of acetic acid in the solution and pressure were varied. The percentage of CF_3H in the total of the two gases rose as the mol ratio of hydrogen fluoride to acetic acid decreased from 150 to 100 but then decreased as this was lowered to 15 at atmospheric pressure. At three atmospheres, pressure concentration had little effect but the percentage of CF_3H decreased to about one third of its value at atmospheric pressure. Other factors such as the "age" of the electrodes influenced the results and it was not feasible to study these in detail.

Propionic acid.—A similar large scale operation was performed with propionic acid in cells of Type C. A total of 10 kg. of purified ethforane

was prepared in this manner. The current density was 0.04 amperes per sq. cm. for 200 amperes and the voltage was 5.5 to 7.0. The gas stream analyzed in volume percentage: H_2, 80; CO_2, 11; OF_2, 2.6; CF_4, 0.9; C_2F_6, 5.4; C_2F_5H, 0.9; and $C_2F_4H_2$, 0.1. A preliminary examination of the cell contents at the conclusion of the experiment indicated the presence of fluorine containing propionic acids.

Butyric acid.—A cell of Type B was used at a temperature of −3°. It carried from 100 to 200 amperes. The voltage was 5.3 at 100 amperes with a current density of 0.0047 ampere per sq. cm. The total initial charge was 50.5 mols of butyric acid and 1375 mols of hydrogen fluoride. Hydrogen fluoride was added periodically to maintain an operating level in the cell. A total of 1278 faradays was passed and there were obtained 526 mols H_2, 44.0 mols CO_2, 10.7 mols OF_2, and 5835 grams of fluorocarbon product. Of this, 21 per cent boiled below −38° and consisted of CF_4,

TABLE I

Fraction	Boiling range	Weight	Ave. molecular weight
	°C	grams	
1	Below 15	6	162
2	15–18	12	159
3	18–20	12.3	160
4	20–22	17.1	164
5	22–23	14.5	171
6	23	14.5	171
7	23–25	10.0	181
8	25–28	5.5	—
9	28–33	7.1	181
10	33–36	4.2	192
11	36–38	7.5	195
12	38–38	9.4	193
13	38–39.5	19.0	190
14	39.5	17.5	187
15	40–45	4.5	186
16	45–50	2.5	201
17	Residue	11.0	—

C_2F_6, CF_3H, and C_2F_5H, 36 per cent boiled at −38° and was C_3F_8, 3 per cent boiled between −38 and −17, 22 per cent boiled between −17 and −4 and was shown to be C_3F_7H. This was identified by its determined molecular weight 173 (theory 170) and its hydrogen content (1) 0.55 per cent (theory 0.59) and by conversion to the bromide and the chloride (2). Eighteen per cent boiled above −4°. About one third of this was $C_3F_6H_2$ as shown by its determined molecular weight 156 (theory 152) and the hydrogen content 1.29 per cent (theory 1.32). One third of this 18 per cent boiled over 13°. Two hundred grams on distillation through an efficient laboratory column showed the results indicated in Table I.

Adipic acid.—Six cells of Type A were each charged with 200 grams (1.25 mols) of adipic acid and 300 grams (15 mols) of hydrogen fluoride. One hundred and sixty grams of adipic acid were added during the experiment but about 600 grams unreacted material were recovered at its termination. Voltages between 6 and 8 allowed the passage of 3.5 amperes through each cell. A total of 407 grams of fluorocarbon product were condensed from

the gases in the holder with liquid air. Distillation of a portion of this material showed the pattern indicated in Table II.

It is evident that the greatest proportion of this material occurs in the range of the butforane.

Sebacic acid.—A charge of 800 grams of hydrogen fluoride was placed in cell of Type A. It was dried by passing a current through the cell and then 160 grams of sebacic acid added. Bubblers of alkaline KI (to remove OF_2 and CO_2) and sulfuric acid and then a solid carbon dioxide trap to catch high boiling products followed the sodium fluoride tubes in the gas purifying train. The gas stream was periodically analyzed for CO_2 and OF_2.

TABLE II

Boiling range	Weight	Molecular weight
°C	*grams*	
−160 to −38	55	177 average
−38 to −6.5	42	193 average
−6.5 to −2	131	230–238
−2 to +15	37.4	234–235
15 to 24	8.8	
24 to 29.2	26.5	251–270
29.2 to 33.8	22.8	276–290
33.8 to 35.2	6.7	289
35.2 to 40	3.9	283
40 to 54	6.0	
54 to 64	4.6	294
64 and over	12.3	

TABLE III

Boiling range	Weight	Molecular weight
°C	*grams*	
Up to 28	2	
28 to 30	14	285–291
30 to 102	23	
102 to 104	15	443
104 to 120	13	
120 to 127	16	480
127 and higher	16.5	

At 0° the current varied between 3 and 4.5 amperes at voltages between 5.2 and 6. During the experiment 820 grams of hydrogen fluoride and 73 grams of sebacic acid were added. A total of 26 faradays were passed.

The products were recovered from three places. The gas holder contained 260 liters which were chiefly hydrogen. A liquid air condensate of this gave 25 grams of fluorocarbons of which half were methforane and the remainder had a molecular weight varying from 100 to 200. Dry air was passed through the cell as it was warmed from 0° to 96° and the gases passed through sodium fluoride and condensed in solid carbon dioxide. Thirty-five grams of fluorocarbons were recovered from this source. A cell residue of 130 grams after the removal of hydrogen fluoride showed 16.3 per cent fluorine by weight. A total of 64 grams of liquid fluorocarbons were found

in the solid carbon dioxide traps and, combining the higher boiling material from the gas holder, a total of 99.5 grams liquid fluorocarbons were obtained. The distillation pattern of this is of interest in showing a predominance of five, eight, and nine carbon fluorocarbons.

A total of 8.6 grams of OF_2 and 29 grams of CO_2 were also produced.

Other acids—pivalic, benzoic, fencholic, phenylacetic, and cyclohexylacetic.—Other carboxylic acids were employed, the following being examples. One hundred and eighty-two grams of fluorocarbons were obtained from pivalic acid, over one third of which were butforane with methforane, ethforane, and pentforane in significant amounts. Benzoic acid gave fluorocarbons chiefly in the range of six and seven carbon atoms. Fencholic acid gave a higher boiling product. The largest fraction, b.p., 114°–117°;

TABLE IV

Boiling range	Weight	Molecular weight
°C	*grams*	
CF_2	50	
C_2F_6	5	
−78 to −22	14	100–128
−22 to −3	7	128–189
−3 to +30	8	188–260

TABLE V

Boiling range	Weight	Molecular weight
°C	*grams*	
28 to 30	8.4	288
46 to 54	8.2	310
54 to 56	5.4	318
56 to 58	7.4	328
hold up	2	

mol. wt., 457; C, 23.2 per cent; F, 75.3 per cent; (theory, mol. wt., 450; C, 24%; F, 76% for C_9F_{18}). Phenylacetic acid also produced fluorocarbons. The one major fraction had mol. wt., 348; b.p., 74°–77° and analyzed 75 per cent F and 23 per cent C; another, b.p., 95°–97°; mol. wt., 407; 75.1 per cent F; 23.4 per cent C. They apparently are cyclic fluorocarbons of seven and eight carbon atoms. Cyclohexylacetic acid gave about the same products.

Type A cells were employed for all following experiments.

Methanol.—The cell was charged with 750 grams of hydrogen fluoride and 35 grams of methanol. A total of 9 faradays gave 16 grams of a mixture of CF_4 and CF_3H in a ratio of 3 to 2 as determined by molecular weights and fractionation.

Ethanol.—The fluorocarbon products found were as shown in Table IV for the passage of 21.2 faradays and the use of 2 mols of ethanol.

Phenol.—The passage of 11.8 faradays through a solution of 200 grams phenol in 980 grams hydrogen fluoride produced 32.7 grams of fluorocarbons. No low boiling materials were found. The product appeared to be

fluorocarbons containing five and six carbon atoms as the distillation pattern showed (Table V).

Ethers.—Ethers are very satisfactorily employed in this process. Diethyl, ethyl-n-propyl, and di-n-butyl ethers all gave fluorocarbon products boiling over a long range.

ACKNOWLEDGMENT

The work of Part IV was done under the sponsorship of the Minnesota Mining and Manufacturing Company.

REFERENCES

1. W. H. Pearlson, T. J. Brice, and J. H. Simons, *Ind. Eng. Chem., Anal. Ed.*, **18**, 330 (1946).
2. T. J. Brice, W. H. Pearlson, and J. H. Simons, *J. Am. Chem. Soc.*, **68**, 968 (1946).

V. From Hydrocarbons

J. H. Simons and R. D. Dresdner

ABSTRACT

Previous work has shown that fluorocarbons can be produced by a direct electrochemical method from solutions of various organic compounds in liquid hydrogen fluoride. Hydrocarbons are not very soluble in hydrogen fluoride and the solutions are not electrically conducting. It has been found, however, that fluorocarbons can be produced from hydrocarbons by this process provided that another substance is added to make the solution conducting. A wide variety of substances can be used for this purpose and they have been tried in combination with a number of hydrocarbons. Experiments using n-octane and various addends are reported, both organic and inorganic. The chief product from octane was octforane.

INTRODUCTION

Previous parts of this paper have shown that fluorocarbons could be produced by a direct electrochemical method from solution of a variety of organic compounds in hydrogen fluoride. The solubility of hydrocarbons in hydrogen fluoride is low and the solutions are not electrically conducting. It has been found, however, that despite these facts fluorocarbons could be produced from hydrocarbons by this process, provided that another substance was added to give conductivity to the electrolytic solution. It was found that a wide variety of substances could be used for this purpose and a number of hydrocarbons were used. We report here experiments using n-octane. Other hydrocarbons, such as toluene, dodecane, tetradecane, and iso-octane, were used. The selection of octane for more extensive study was made because of its boiling point. At 0° and atmospheric pressure its vapor pressure is sufficiently low so that losses by vaporization are not excessive. Also, the products formed are sufficiently volatile under the same conditions so that the major portion of them escape with the hydrogen from the cell and can be conveniently caught in cold traps.

EXPERIMENTAL

Cells of Type A (described in Part IV of this paper) were used for these experiments and the technique previously reported was followed.

Octane with water.—The original cell charge was 160 grams n-octane, 550 grams HF, and 10 grams H_2O. Water and hydrogen fluoride were added periodically as the experiment progressed, the hydrogen fluoride to maintain the liquid level and the water to provide conductivity. The total of these additions amounted to 440 grams of hydrogen fluoride and 60 grams of water for the passage of 47.3 faradays. Five hundred and sixty liters of gas not condensed at −70°C were produced. From this 54 grams of CF_4, methforane, and 27 grams of C_2F_6, ethforane, were condensed in liquid air. One hundred and twenty grams of product were collected in solid carbon dioxide traps during the experiment and 14 grams by passing dry air through the cell at its conclusion (Table I).

TABLE I

Boiling range	Weight	Mol. wt.	F
°C	*grams*		%
−70 to 0	9		
0 to +30	7		
30 to 37	14.5	221–292	
37 to 52	3	285–303	
52 to 55	6.5	303–331	
55 to 70	6.5	330–335	79.1, 77.4
70 to 75	3.0	341	
75 to 85	4.0	381	
85 to 90	3.0	374	
90 to 95	11.0		
95 to 96	52.5	440–444	78.6
Higher boiling	5.5	(b.p., 102–103)	
Losses	6.5		

The original fractions contained two layers when chilled. The upper one was hydrocarbon but it was relatively small in amount (about 5%). It was removed by chilling at −80° and removing with a capillary pipette. A constant boiling mixture of octane and octforane boiling at 95°–96° was in evidence. After separation of the hydrocarbon and redistillation, the material of the original fractionation boiling above 90° was found to boil at 102°–103° and to be C_8F_{18}, octforane, in an amount of about 70 grams.

A cell residue was found (50 grams) which was soluble in base and had a fluorine content of 13.4 per cent. It behaved as an acid with an equivalent weight of 322.

In order to find out how much water the process would tolerate, the cell was charged with 600 grams HF, 15 grams H_2O, and one mol of octane. Analyses for CO_2 and OF_2 in the gas stream were taken periodically. The cell was operated until fluorocarbon appeared in the cold trap. During this period OF_2 was 0.04 g./l. or less, and CO_2 was 0.06 to 0.08 g./l. of gas. Ten faradays were passed and a further 10 grams of water were added to maintain conductivity. It brought the water concentration of the solu-

tion to 4.5 per cent. An addition of 50 grams of water raised its concentration to 13.5 per cent. The OF_2 concentration then decreased to zero and the CO_2 concentration increased to 0.1 g./l. This CO_2 concentration represents 30 per cent of the theoretical for complete oxidation of the hydrocarbon. Water was progressively added until its concentration was 40 per cent. The CO_2 concentration rose to 0.21 g./l. or 65 per cent of theoretical for complete oxidation of the hydrocarbon. Little fluorocarbon was produced at the higher water concentrations.

Octane and methanol.—To 800 grams of HF in the cell, which had been dried by the passage of current, 15 grams of methanol and 25 grams of octane were added. During the experiment an additional 23 grams of methanol, 400 grams of HF, and 15 grams of octane were added. OF_2 was small at the start but soon dropped to zero. CO_2 varied considerably, rising to high values just after the addition of methanol. In one case it was 21 per cent. Other high values of 18 and 10 per cent were found. Of the gaseous products condensed in liquid air, 22 grams of CO_2 were found and 14 grams of gaseous fluorocarbons of which 65 per cent was CF_4. The condensate in the solid carbon dioxide trap was 45 grams of fluorocarbon and 8 grams of octane. Seven grams of fluorocarbons were recovered from the cell. Of the liquid fluorocarbons, 35 grams were octforane, b.p., 102° to 104°, mol. wt., 443. No polymerized material was found in the cell. Twenty-one faradays were passed in this experiment.

Octane and acetic acid.—A charge of 800 grams of electrolytically-dried HF, 15 grams of acetic acid, and 25 grams of octane was used. Forty grams of acetic acid and 16 grams of octane were added as the experiment proceeded; 14.4 faradays were passed. CO_2 showed an average concentration in the gas stream of 10 per cent and OF_2 of 0.030 g./l. The products condensed in liquid air amounted to 80 grams of which 32 were probably CO_2. This material was inadvertently lost before further identification could be made. A total of 22.5 grams of fluorocarbons boiling above room temperature were obtained, 65 per cent of which were in the C_8F_{18}, octforane, boiling range.

Octane and pyridine.—The initial charge consisted of 900 grams HF, which were electrolytically dried, 28 grams octane, and 10 grams pyridine. Twenty grams pyridine were added during the passage of 13.9 faradays. From the collected gas a liquid air condensate of 20 grams was obtained which was chiefly NF_3 with some CF_4. As both NF_3 and CF_4 have appreciable vapor pressures at liquid air temperature, a liquid air condensate does not represent the total production of these materials.

A total of 81 grams of fluorocarbons boiling above −70° was obtained. Of this 25 grams boiled at 29°–31°, pentforane and 28 grams boiled at 101° to 103°, octforane.

2-Fluoropyridine was employed to impart conductivity in place of pyridine with the hope that as it is a more unreactive compound it would resist the action of the process and cause a greater ratio of octane to be used. Within the limits of the experiments, however, its action was very similar. From the passage of 8.4 faradays, 12 grams of liquid air condensate and 73 grams boiling above −70° were obtained. Of this 28.5 grams boiled 28°–30° and had a molecular weight of 288 (C_5F_{12}) while 30 grams boiled 102°–104° and had a molecular weight of 438 (C_8F_{18}).

Octane and sodium fluoride and other inorganic substances.—The charge

consisted of 670 grams of HF, 28 grams of NaF, and 28 grams of octane. After a passage of 10.4 faradays, there were obtained only 3 grams of liquid air condensate. Of the 35 grams of material boiling above −70°C, 27 grams boiled 100°–103° and had a molecular weight of 440 (C_8F_{18}). There was, however, considerable residue found in the cell after the completion of the experiment, a large portion of which was iron and nickel salts; the cell showed signs of corrosion. Although NaF functions and produces a high percentage of one product, it seems less desirable than other substances due to this corrosive effect.

Other substances were employed to give conductivity to the solution, for example, NH_3 and $Hg(CN)_2$, all with the result of the production of octforane but with minor differences in details.

In all cases, however, it is abundantly evident that the process does not consist of the production of fluorine which then rises through a layer of octane residing on the top of the hydrogen fluoride solution, as one might naively assume. The production of such large percentages of octforane would alone prove that this was not the case. Fluorine is not detected in the gas stream which is always the case when it is formed at the anode. When the potential of the cell is raised it reaches a value at which fluorine is produced, but minor explosions occur in the cell, fluorine is detected in the outlet, and the products are the usual ones of the action of fluorine with liquid hydrocarbons, that is, complete fragmentation. The process is operated under conditions where this does not occur.

ACKNOWLEDGMENT

The work of Part V was done under the sponsorship of the Minnesota Mining and Manufacturing Company.

Any discussion of this paper will appear in the discussion section of Volume 95 of the TRANSACTIONS of the Society.

CHEMICAL PROOF OF THE PRESENCE OF CHLORINE IN BLUE FLUORESCENT ZINC SULFIDE[1,2]

F. A. KROEGER AND J. E. HELLINGMAN

Philips Research Laboratories, N. V. Philips Gloeilampenfabrieken, Eindhoven, Holland

ABSTRACT

Chemical determinations of the chlorine present in phosphors support a previously enunciated theory of blue centers.

In order to prove the theory that chlorine plays an essential role in the formation and construction of blue centers (1), the authors carried out actual chemical determinations of the chlorine content of the phosphors.

Zinc sulfide heated in an atmosphere containing HCl is always contaminated by some superficial $ZnCl_2$ that adheres to the crystals. However, only that chlorine is of interest which is incorporated in the interior of the crystals. For this reason, all powders have to be washed very carefully before the actual determination is started, in order to free them of these mechanical chloride contaminations. To this end, portions of about 10 grams of the sulfides were stirred into about 100 ml. of chlorine-free water and heated on a water bath for several hours. After cooling, the sulfide was filtered and dried at 80°C. This treatment was repeated about fifty times. Even after the last wash, the water was not entirely free from chlorine. This must be attributed to the fact that ZnS is slightly soluble in water. The chlorine found, therefore, must have been incorporated chlorine which dissolved along with the sulfide.

For the determination of chlorine, about one-half gram of the washed products was brought into solution by heating with 0.4 ml. of $4N$ HNO_3. The sulfur formed by oxidation of H_2S agglomerated at the surface, leaving a clear solution. After filtration, 4 to 5 drops of a 1 per cent $AgNO_3$ solution were added, the solution heated to boiling, and then let cool for about one-half hour. The precipitate of AgCl was then compared nephelometrically with standards of known chlorine content, prepared in the same manner, but using chlorine-free zinc nitrate instead of ZnS. The results are accurate to about ± 50 per cent.

Table I shows the chlorine content found for different samples of ZnS heated in H_2S, H_2S + HCl, H_2, and H_2 + HCl, together with the intensities of the blue fluorescence taken from our previous paper (1). The ZnS used was a material made by Orr (England) which was first dechlorinated by heating for two hours in a stream of hydrogen at 1050° C.

It is seen that even our dechlorinated ZnS was not entirely free from chlorine, but still contained 2.10^{-5} gram atoms Cl/mole ZnS. The amount of chlorine present in the products heated in atmospheres containing HCl tends to increase with the partial pressure of the HCl. The intensity of

[1] Addendum to the paper by F. A. Kroeger and J. E. Hellingman, *J. Electrochem. Soc.*, **93**, 156 (1948).

[2] Manuscript received November 10, 1948. This paper prepared for delivery before the Philadelphia Meeting, May 4 to 7, 1948.

fluorescence increases likewise. There are some discrepancies, but in view of the difficulties involved in the determinations these are not disturbing.

The chlorine content agrees reasonably well with the values of the concentration of blue centers estimated from current saturation data by Bril (2), and with those arrived at by the authors from a comparison of the intensity of fluorescence with that of ZnS:AgCl. The absence of fluorescence in the products which were heated in H_2S or H_2, yet contained chlorine, may be explained in two ways. In the first place, the fluorescence must be expected to be weak if the concentration of fluorescence centers is smaller than the concentration of quenching centers. In particular, this will be true if the quenchers not only absorb part of the exciting radiation but if, in addition, they are excited by energy transferred from the fluorescence centers, as is the case in zinc sulfide (3).

TABLE I

Atmosphere of preparation (1200°C.)	Intensity of blue fluorescence under 2537 Å	Chlorine content	Estimated concentration of centers	
			Bril (2)	Authors
		grams atoms Cl/mole ZnS		
H_2S	0	2×10^{-5}		
$H_2S + 10\%$ HCl	6	4×10^{-5}		
$H_2S + 20\%$ HCl	20.5	7.5×10^{-5}	3×10^{-5}	
$H_2S + 40\%$ HCl	39	6×10^{-5}	8×10^{-5}	
HCl	100	27×10^{-5}	$>30 \times 10^{-5}$	10^{-5} to 10^{-4}
H_2	0	2×10^{-5}		
$H_2 + 10\%$ HCl	28.5	7.5×10^{-5}		
$H_2 + 20\%$ HCl	49	7.5×10^{-5}		

In the second place, the chlorine found may well have been incorporated in the innermost parts of the crystals. The centers formed by it escape excitation because the ultraviolet radiation is absorbed mostly near the surface. This situation is quite plausible, for the products were made from a sulfide containing chlorine by heating it in hydrogen, a treatment which will dechlorinate especially the surface regions of the particles. On the whole we believe that the present results lend strong support to our model of the blue centers.

ACKNOWLEDGMENT

We are indebted to Dr. A. Claassen, of the analytical department of this laboratory, under whose supervision the chlorine determinations were carried out.

Any discussion of this paper will appear in the discussion section of Volume 95 of the TRANSACTIONS of the Society.

REFERENCES

1. F. A. KROEGER AND J. E. HELLINGMAN, *J. Electrochem. Soc.*, **93**, 156 (1948).
2. A. BRIL, "On the saturation of fluorescence with cathode ray excitation," to be published in *Physica*.
3. F. A. KROEGER, "Some Aspects of the Luminescence of Solids," Chapter VI, Elsevier Publishing Co., Amsterdam-New York (1948).

ON THE FLUORESCENCE OF ATOMIC SILVER IN GLASSES AND CRYSTALS[1]

W. A. WEYL

Department of Mineral Technology, The Pennsylvania State College, State College, Pennsylvania

AND

J. H. SCHULMAN, R. J. GINTHER, AND L. W. EVANS[2]

Naval Research Laboratory, Washington, D. C.

ABSTRACT

Metal atoms represent a group of fluorescence centers which have the advantage of known structure. Due to their neutrality, they are not affected very strongly by their environment. The following methods have been developed for producing atomic silver in glasses and crystals.

1. Thermal dissociation of silver oxide.
2. Reduction of silver ions by means of hydrogen.
3. Reduction of silver ions by electron bombardment.
4. Reduction of silver ions through exposure to x-rays.

Experiments are described which deal with the formation of fluorescence centers of Ag^+ ions present in alkali halides and glasses. The fluorescence properties of these simple systems will be described.

INTRODUCTION

Precise information concerning the fluorescence phenomenon is limited to those systems where the fluorescence centers are sufficiently separated from other molecules and ions so that their electronic transitions are not perturbed by electric fields. Atoms of rare gases and of metals, such as sodium and mercury, represent the simplest types of fluorescent centers. In the gaseous state under sufficiently low pressure, these atoms are energetically isolated and, as a result, they exhibit resonance fluorescence, emitting a spectrum of discrete lines. These lines represent the permitted transitions between the ground state and various higher energy levels of electronic excitation. In condensed systems, however, the electronic transitions are strongly influenced by adjacent molecules, so that the interpretations of light absorption and emission become very difficult.

Metal atoms as activators of fluorescence in condensed systems received considerable attention when A. Schleede (1937) explained the blue fluorescence of certain preparations of ZnO and ZnS on the basis of zinc atoms in excess over the stoichiometric ratio. Pure zinc oxide obtained by thermal decomposition of the carbonate did not fluoresce at room temperature. Heating under reducing conditions, or treatment with vapors of metallic zinc, was found to produce blue fluorescence. At the same time W. A. Weyl discovered that fluorescent glasses could be obtained with atomic silver as activator. This work has been continued and extended to a num-

[1] Manuscript received August 23, 1948 (abstract received February 27, 1948). This paper prepared for delivery before the Columbus, Ohio, Meeting, April 14 to 17, 1948.

[2] Present address: Sylvania Electric Products, Inc., Emporium, Pennsylvania.

ber of alkali halides with atomic silver as fluorescence centers. It is the object of this paper to describe a number of phosphors, both crystalline and glassy, which are activated in this way, as well as several different methods for producing the activation. Studies of these phosphors may help to shed more light on the interaction between activators and host lattice. Furthermore, they are of interest with respect to photographic processes, since their formation, by one of the procedures to be described, involves a process which resembles that of formation of the photographic latent image.

Something should be said at this point about the terms "silver atom" and "atomic silver" which are used in this paper. Excess zinc in the previously mentioned ZnO and ZnS phosphors, while commonly spoken of as interstitial zinc atoms, may perhaps be better described as interstitial zinc ions with electrons trapped in the field of these ions. There is evidence that the "orbits" of these trapped electrons may extend over several interatomic distances, in contrast to the much smaller orbits of the electrons in a free zinc atom. Furthermore, the absorption spectrum of these trapped electrons and the energy required to remove them into the conduction band of the crystal are considerably different from the absorption spectrum and the ionization potential of the isolated atom. As another example, the excess alkali metal "atoms" (F-centers) in alkali-halide crystals colored by exposure to alkali metal vapor are more correctly described as a system of alkali metal ions surrounding a halogen-ion vacancy which has trapped an electron. The trapped electron is shared among the alkali metal ions adjacent to the vacant halogen-ion position and, at any given time, one or the other of these alkali ions plus the trapped electron may be looked upon as an alkali metal atom. In some of the "atomic silver" activated alkali halide phosphors we shall describe, the situation may be analogous to this, the "silver atoms" being electrons trapped at a vacant halogen-ion site which has one or more silver-ion neighbors. In this case the electron might be more closely associated with the silver than with the alkali ions surrounding the vacancy. On the other hand, in silver-bearing silicate glasses formed by quenching from high temperatures, consideration of the silver as a "frozen-in vapor" of silver atoms may be quite correct. The terms "atomic silver" and "silver atom" are, therefore, used in this paper merely as a convenient designation, in the same way that it has become customary to speak of interstitial zinc "atoms" in zinc oxide and sulphide phosphors, and of excess sodium "atoms" in colored NaCl crystals.

METHODS OF PRODUCING ATOMIC SILVER IN GLASSES AND CRYSTALS

Thermal dissociation

Silver oxide introduced into a soda-lime-silicate glass can participate in the glass structure. Silver ions, as well as the similar sodium ions, assume interstitial positions. Glasses containing silver ions are colorless and do not fluoresce when irradiated with the 3650 Å mercury line.

However, if the concentration of silver oxide exceeds approximately 0.2 to 0.5 per cent, a part of the silver oxide dissociates to form metallic silver. The solubility of silver metal in such a glass is very low and, as a result, the silver is precipitated in the form of droplets and microscopic crystals when

the glass melt is cooled. Depending upon the size of the crystals, the color of such a glass will vary from yellow to brown and gray. Needless to say, this crystalline silver does not fluoresce.

Between these two extremes, true Ag^+ ions and condensed metallic Ag, there is a stage where a noticeable amount of silver atoms is formed, but where the concentration has not yet exceeded the solubility limit of silver in glass. As the solubility of metals in glasses increases with increasing temperature, the best results are obtained by melting the glass at relatively high temperatures (1450°C.) and chilling the molten glass by pouring it into water. Under these conditions a melt containing about 0.2–0.5 per cent Ag_2O produces a strongly fluorescent glass. The fluorescence centers are silver atoms which did not have time to diffuse and to aggregate into crystals. The "frozen in" silver vapor emits white light when exposed to 3650 Å radiation.

From the description of this experiment, it is evident that the method of producing atomic silver by thermal dissociation is very difficult to control. The diffusion of neutral silver atoms, due to their lack of chemical bonds, is very fast. An extremely high rate of cooling is required to prevent their aggregation. Even if only a small fraction of the silver precipitates, the glass assumes a yellow-brown color which impairs the fluorescence. Furthermore, the dissociation equilibrium of the silver oxide depends strongly on the composition of the glass. Whereas soda-lime-silicate glasses cannot keep in solution much more than 0.2 per cent Ag_2O, certain phosphate glasses dissolve more than 10 per cent Ag_2O without noticeable dissociation. In order to study, under more controlled conditions, this interesting phosphor—silver atoms distributed in a glassy matrix—new methods were developed.

Reduction of the silver ions by means of hydrogen

It has been found that soda-lime-silicate glasses containing about 0.2 per cent Ag_2O can be reduced by hydrogen gas at a temperature of about 100°C. While the diffusion of hydrogen into the glass is slow at this temperature, it is faster than the speed of aggregation of the atomic silver formed. In order to enhance diffusion of the hydrogen into the glass, the latter is employed preferably in the form of a powder. If the powder is sufficiently fine, reduction at 100°C. can be completed within a few hours. Under the same conditions, glass rods 1 mm. in diameter require about two weeks. Under 100°C. the diffusion rate of the silver atoms is still negligible, the glass therefore remains colorless, but due to the formation of silver atoms it becomes fluorescent under near ultraviolet (U.V.) excitation. This method is not applicable to all glass compositions. Phosphate glasses, for example, require a reduction temperature too high for keeping the silver atoms isolated.

Reduction of silver ions by electron bombardment

The exposure of a glass or alkali halide crystal containing silver ions to electron bombardment produces atomic silver according to:

$$Ag^+ + \Theta = Ag$$

This implies that any silver ion in the structure can be reduced to give a luminescent center of atomic silver. As mentioned in the "Introduction,"

an alternative description of the phenomenon in alkali-silver halide crystals may be:

$$Cl^- + Ag^+ \text{ (neighbor to a } Cl^- \text{ vacancy)} + \text{energy from bombarding electron} \rightarrow Cl^0 + Ag^0 \text{ (= electron trapped in } Cl^- \text{ vacancy next to } Ag^+ \text{ ion).}$$

The neutral Cl^0 may then move to the surface of the crystal by hole migration and escape as free chlorine. This scheme implies that only specially situated silver ions are reduced to give luminescent atomic silver centers.

The cathode-ray bombardment method has the advantage that it is applicable at room temperature where the aggregation of silver atoms is negligible. Exposure of a sample to electron bombardment does not have much depth action, however. Alkali halide crystals, both with and without silver, are discolored by exposure to cathode rays (F-center formation). The F-center coloration can be bleached out by irradiation with visible light, without destroying the fluorescence response to near ultraviolet excitation created by the cathode-ray bombardment.

Reduction of silver ions through exposure to x-rays and other radiations

The exposure of glasses and crystals containing silver ions to x-rays was found to be a suitable method for producing atomic silver. In principle, this method is identical with that described above, except that the energy source is different, and the effect is not limited to the surface layer. Absorption bands in the visible, due to F-centers, are likewise found here in the alkali halides, with or without silver.

It was also found that radiations of lower frequency than x-rays are capable of developing response to long wave ultraviolet in some of the Ag-activated materials. A sample of NaCl containing 5 mol per cent of AgCl, for example, does not respond to 3650 Å excitation. After exposure to the radiation from an unfiltered low pressure mercury discharge lamp with quartz envelope (1850 and 2537 Å radiation) for one hour at room temperature, a quite marked response to 3650 Å excitation is observed, the luminescence being similar in color to that found after x-ray treatment.

EXPERIMENTAL PROCEDURE

1. The alkali-silver halides were prepared by melting the mixture of the two salts in silica or platinum crucibles and stirring with a platinum rod. The melt was quenched by pouring it into a silver dish which was cooled by water. This procedure was adopted to avoid possible exsolution of the mixed crystals, especially in the regions of high silver concentrations.

2. The glasses were melted from the mixture of the constituents in kyanite crucibles in a globar furnace. By introducing a part of the alkali in the form of the nitrate, oxidizing conditions were maintained. The silicate glasses were of the soda-lime type. They contain 0.2 per cent Ag_2O introduced in the form of the nitrate.

The group of phosphate glasses studied had the following composition: Al metaphosphate, 50 per cent; Ba metaphosphate, 25 per cent; and K metaphosphate, 25 per cent.

To this mixture silver phosphate was added up to 16 per cent. All glasses remained clear (1, 2, 4, 8, 12, and 16% Ag_3PO_4).

3. Fluorescence of all specimens was observed under two different types of ultraviolet lamps.

a. A low pressure mercury vapor lamp (Mineralight), combined with a Corning 9863 filter. The radiation of this lamp is predominantly in the region of the 2537 Å line and will be characterized by this wave length.

b. A high pressure mercury lamp with Corning 9863 filter, giving peak intensity in the region of the 3650 Å mercury line. For the same region a "360 B.L." fluorescent lamp with a purple envelope (Sylvania Electric Products) was used. Observations under both these lamps are characterized by the dominant wave length 3650 Å.

4. X-ray treatment of the samples was effected by exposing them to the radiation of a Cu-target Be-window G.E. x-ray tube, operated at 40 kvp. and 15 ma., for five minutes at a window-to-sample distance of two inches.

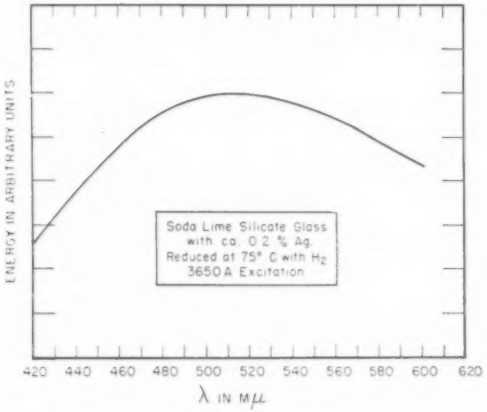

ENERGY IN ARBITRARY UNITS
Soda Lime Silicate Glass
with ca. 0.2 % Ag.
Reduced at 75° C with H_2
3650A Excitation
420 440 460 480 500 520 540 560 580 600 620
λ IN mμ

FIG. 1

5. Electron bombardment of the samples was effected by exposing them to a cathode ray beam in a special demountable cathode ray tube. The voltages used were about 1 kv. or higher. Current measurements could not be made at the time.

EXPERIMENTAL RESULTS

Silver activated silicate glasses

As stated before, no more than approximately 0.2 to 0.5 per cent Ag_2O can be incorporated into a soda-lime-silicate glass without producing color through precipitation of metallic silver (thermal dissociation of the oxide). These glasses do not fluoresce under 2537 Å or 3650 Å radiation. The best results were obtained with this group of glasses, when the fine powder was reduced by means of hydrogen gas at a temperature of about 100°C. A white fluorescence resulted when the reduced glass was exposed to 3650 Å radiation. The fluorescence efficiency decreases with increasing temperature (of observation) and disappears at 350°C. Short periods of heating

will not permanently destroy the fluorescence. However, a treatment of the glass at 300°C. for 15 hours kills the fluorescence permanently. Under these conditions, the silver atoms find sufficient time for aggregation.

The emission spectrum of a soda-lime-silicate glass containing 0.2 per cent Ag_2O, after reduction by hydrogen gas, is given in Fig. 1. It is a broad continuous emission band extending throughout the visible.

Phosphate glasses

The complex Al-Ba-K metaphosphate glass offers the advantage that up to 16 per cent silver phosphate can be introduced without precipitation of

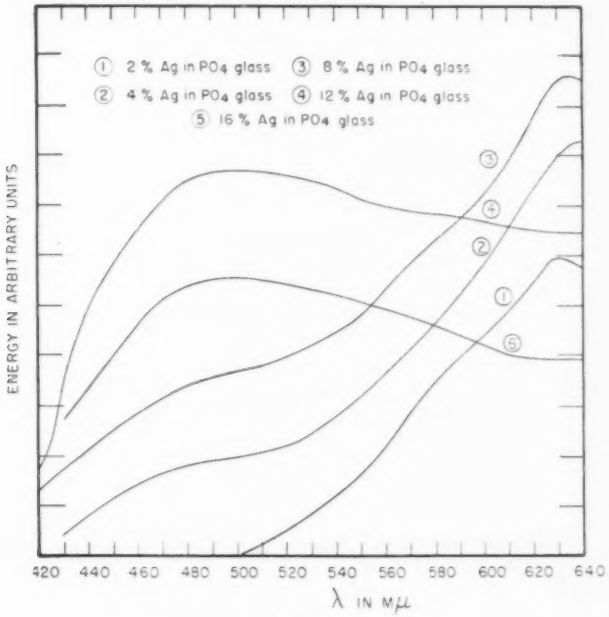

① 2 % Ag in PO4 glass
② 4 % Ag in PO4 glass
③ 8 % Ag in PO4 glass
④ 12 % Ag in PO4 glass
⑤ 16 % Ag in PO4 glass
ENERGY IN ARBITRARY UNITS
420 440 460 480 500 520 540 560 580 600 620 640
λ IN MμL

FIG. 2

silver. The strong forces which hold the Ag^+ ions in the structure of the phosphates make it impossible to apply the chemical reduction by means of hydrogen gas in a temperature region which excludes diffusion and aggregation of the silver atoms. These glasses, however, are suitable for reduction by means of x-rays and by cathode rays.

Phosphate glasses containing silver ions show a weak blue fluorescence when exposed to 2537 Å radiation. Under the 3650 Å lamps, they do not fluoresce.

Fig. 2 shows the emission spectra under 3650 Å excitation, after exposure to x-rays, of a number of phosphate glasses containing various percentages of silver phosphate. The fluorescence is orange to yellow; it appears that

increasing Ag concentration causes the growth of a new fluorescence emission band at shorter wave lengths. This is rather unusual, since in most phosphors increase in activator content shifts the emission to longer wave lengths or causes the build-up of a new band at longer wave lengths.

The glasses after x-ray treatment show the same weak response to 2537 Å radiation.

Alkali halides

Fluorescence of silver ions.—Alkali halides and silver halides can form mixed crystals, at least to a limited extent. In the NaCl–AgCl mixed

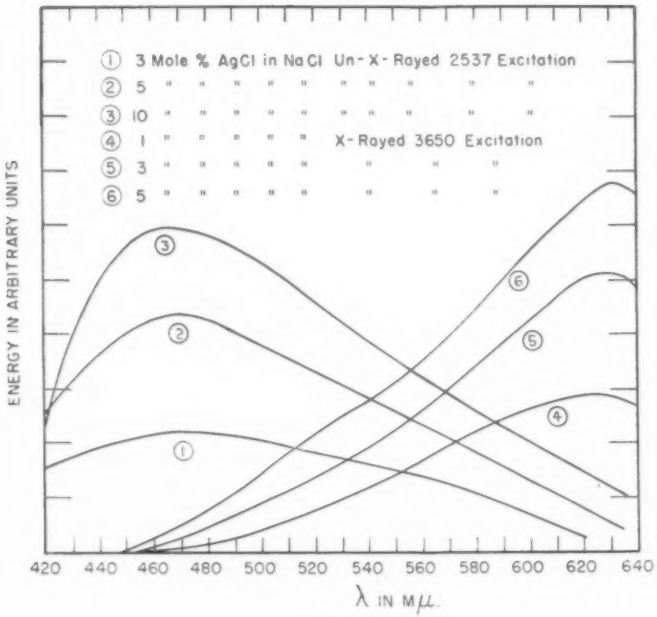

① 3 Mole % AgCl in NaCl Un-X-Rayed 2537 Excitation
② 5 " " " " " " " " " "
③ 10 " " " " " " " " " "
④ 1 " " " " " X-Rayed 3650 Excitation
⑤ 3 " " " " " " " " "
⑥ 5 " " " " " " " " "
ENERGY IN ARBITRARY UNITS
420 440 460 480 500 520 540 560 580 600 620 640
λ IN MμL

FIG. 3

crystal an occasional Na^+ of the NaCl structure is replaced by an Ag^+ ion which has about the same size and has identical charge. These Ag^+ ions distributed in NaCl crystals can be excited to fluoresce by irradiation with the 2537 Å line, while they do not fluoresce under long wave ultraviolet (3650 Å), if the Ag^+ concentration is low. The fluorescence emission of silver ion activated sodium halides covers a region from the near ultraviolet into the visible, with a subjective fluorescence color of blue. The peak of the emission depends on the anion (chloride, bromide, and iodide) as well as on the concentration of the silver ions.

Potassium halides activated by silver ions were found to be non-fluorescent at room temperature, both under 2537 Å and 3650 Å irradiation.

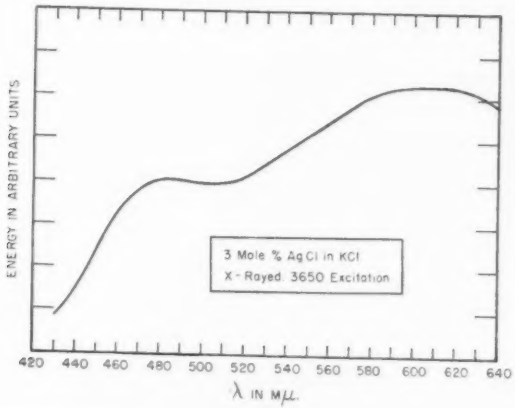


FIG. 4

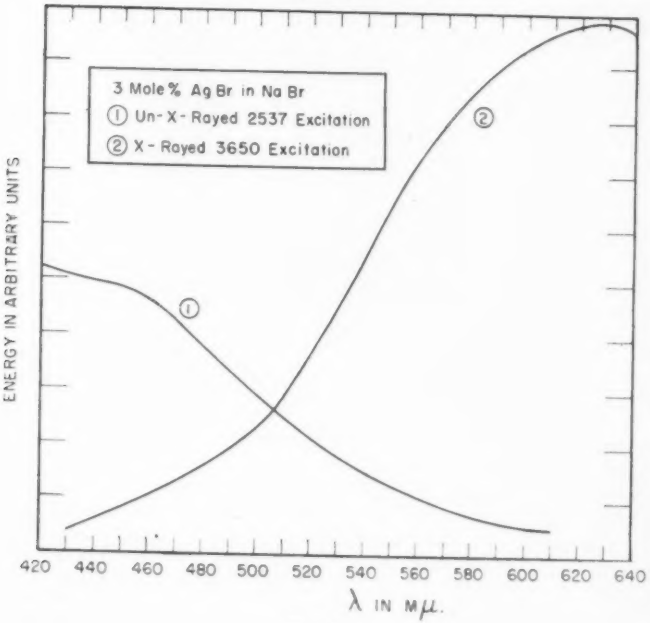

3 Mole % Ag Br in Na Br
① Un-X-Rayed 2537 Excitation
② X-Rayed 3650 Excitation
ENERGY IN ARBITRARY UNITS
420 440 460 480 500 520 540 560 580 600 620 640
λ IN mμ.

FIG. 5

However, phosphors have been obtained which fluoresce under 2537 Å radiation at lower temperatures.

Fig. 3 (curves 1, 2, and 3) shows the spectral distribution of the fluorescence of some untreated NaCl–AgCl phosphors under 2537 Å excitation.

Fluorescence of silver atoms.—Exposure of the NaCl–AgCl mixed crystals to x-rays or to an electron beam produces a new phosphor activated with atomic silver. This "atomic silver" responds to long ultraviolet and produces yellow to pink fluorescence under 3650 Å radiation.

As a result of this treatment of the NaCl–AgCl mixed crystal, the bluish fluorescence under 2537 Å is decreased somewhat in intensity, and the material fluoresces orange under 3650 Å radiation.

Fig. 3 (curves 4, 5, and 6) gives the intensity distribution of the 3650 Å excited fluorescence of various NaCl–AgCl preparations after x-ray treatment.

Fig. 4 gives the emission spectrum of a KCl–AgCl phosphor under 3650 Å excitation, after exposure of the phosphor to x-rays. As in the phosphate glasses there are two peaks observable in the emission spectrum.

Fig. 5 (curve 1) shows the emission of an untreated NaBr–AgBr phosphor

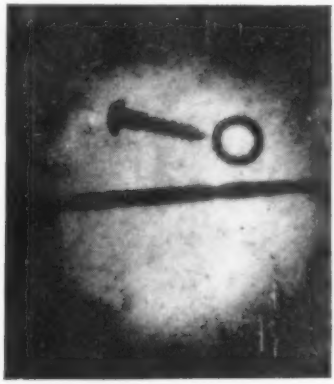


FIG. 6

under 2537 Å excitation, while curve 2 in the same figure shows the 3650 Å excited luminescence of the phosphor after it has been x-rayed.

APPLICATION OF THE X-RAY EFFECT TO RADIOGRAPHY AND X-RAY DETECTION

The fluorescence of NaCl–AgCl or of silver-bearing phosphate glasses after exposure to x-rays can be made use of in radiography. A screen of the phosphor may substitute for the photographic plate. After exposure to x-rays, the image is made visible by irradiating the screen with near ultraviolet radiation. No development is necessary and the screen need not be protected from light at any stage of the process. The speed of such an arrangement has not been developed as yet to the point where it can compete with the photographic film. Fig. 6 shows an x-ray shadowgraph made with a crude NaCl–AgCl screen, using CuK radiation at 40 kv. and 15 ma. from a G. E. beryllium window tube, the window-to-screen distance being one foot and the exposure time being ten minutes. The figure shows the image observed under 3650 Å excitation, after the x-ray exposure was made. The same effect may obviously be made the basis of x-ray detection and dosimetry.

CONCLUSION

There are at present insufficient data at hand to characterize the atomic silver activated glasses and crystals completely. Their formation by thermal dissociation, chemical reduction, and by irradiation processes which are known to have a reducing effect on silver compounds, leaves no doubt, however, that the luminescent centers involve silver atoms in the reduced state.

The simplest concept that may serve to describe these centers is that they are essentially a "frozen-in" vapor of silver atoms, whose energy levels are perturbed by the field of the neighboring ions in the crystal or glass host. The absence of any appreciable afterglow or phosphorescence (visual observation only) is consistent with the hypothesis that the absorption of near ultraviolet serves to raise these atoms to an excited state, without ionizing them, the return to the ground state being accomplished with the emission of fluorescent radiation. Whether these atoms, in the case of the alkali-silver halides, for example, are formed by reduction of silver ions at any lattice position where they replace alkali atoms substitutionally, or whether only those silver ions near halogen-ion vacancies are involved in this change, is not determined. It is hoped that the detailed study of these materials now in progress will make possible a more complete interpretation of these phosphors.

Any discussion of this paper will appear in the discussion section of Volume 95 of the TRANSACTIONS of the Society.

ELECTRODEPOSITION AND ELECTROWINNING OF GERMANIUM[1]

COLIN G. FINK AND VASANT M. DOKRAS[2]

Division of Electrochemistry, Columbia University, New York, New York

ABSTRACT

Aqueous, non-aqueous, and fused electrolytes were studied. The electrodeposition of germanium from aqueous baths is apparently limited to thin flashes of the metal because of the very low overvoltage of hydrogen on germanium. Copper, silver, tin, cobalt, and nickel were each co-deposited with germanium from aqueous solutions. The silver-white inter-metallic compound, Cu_3Ge, was deposited from an alkaline solution. Also described is a method for electrodepositing germanium from a solution of germanium tetraiodide in ethylene glycol and from a fused electrolyte of borax in which germanium dioxide was dissolved. The chemical resistance of the Cu_3Ge plate is good and it may have considerable decorative and protective value.

INTRODUCTION

Until recently, germanium metal was only a chemical curiosity (10). The chemistry of the metal and its compounds was studied by Winkle (1) and by Schwarz (2), and, more recently, by Jaffee, McMullen, and Gonser (10), who reported extensively on sources of the metal, its recovery, and its properties and potential uses. In electrometallurgy, germanium first attracted attention because of its harmful effect in the electrowinning of zinc (3). During World War II, important applications were found for germanium in the field of electronics (4, 5).

Several methods have been reported for recovering the metal: distillation of the finely ground germanium-containing ore with hydrochloric acid to produce $GeCl_4$ contaminated with arsenic (12, 13, 14); reduction of germanium dioxide with hydrogen at 540°C. (16) to produce a powder which is melted under fused NaCl; reduction of the germanium dioxide with carbon or a mixture of carbon and potassium cyanide (18, 10); reaction between zinc and germanium tetrachloride at 930°C. to yield germanium metal containing 0.2 per cent zinc (19).

One instance was found of preparation of the metal by electrolysis of GeO_2 in fused K_2GeF_6 or in molten cryolite in a graphite crucible (10).

Germanium is quite tarnish resistant in air and has remarkable chemical resistance (10). Because all of the common chemical reagents are resisted by the metal, a study of ways for electrodepositing it offered prospects of unusual interest.

Tin and lead are commercially electroplated from alkaline solutions (23)

[1] Manuscript received June 18, 1948. This paper, which was prepared for delivery before the New York Meeting, October 13 to 16, 1948, is adapted from a thesis submitted by V. M. Dokras to Columbia University in partial fulfillment for the degree of Doctor of Philosophy in Chemical Engineering.

[2] Present address: Chandur Rly, Berar, India.

and for the commercial plating of lead the fluosilicate bath is widely used (24). It was expected that germanium could be deposited out of similar solutions.

Hall and Koenig (25) obtained thin, lustrous, and adherent deposits of the metal on copper cathodes from a solution of the dioxide in 3*N* KOH. The deposition stopped, however, after the preliminary film formation, and thereafter only hydrogen was evolved on the cathode. As yet, no one has reported the formation of thick deposits of the metal from any type of aqueous bath.

I. Electrodeposition from Aqueous Solutions

Apparatus.—The experimental apparatus was the usual simple setup using 50 ml. beakers as the electrolytic cells. All of the cathodes used in the experiment were of copper (2 cm. x 2 cm.) polished with medium polishing compound, cleaned, and degreased by standard procedures. It was found inadvisable to use freshly electroplated cathodes, due to the possibility of introducing even a small trace of copper into the bath, which is liable to vitiate the observations as described in the section on the co-deposition of germanium with other metals. The only anodes used were of a special hard carbon, spectrographically free from aluminum, boron copper, iron, tin, magnesium, manganese, silicon, sodium, titanium, vanadium, and lead, and containing only a trace of calcium. The germanium was added to the alkaline solutions in the form of the chemically pure GeO_2 and this GeO_2 was also used in the preparation of other compounds of germanium used during the whole of this investigation.

Deposition from alkaline solutions.—From the alkaline bath of Hall & Koenig (25), containing 2.6 g./l. GeO_2 and 170 g./l. KOH, only thin, preliminary plates were obtained in the temperature range 30° to 90°C. and the GeO_2 concentration range of 2 to 100 g./l. Bath modification through addition of potassium phosphate, potassium citrate, dextrose, or mannitol, or through use of LiOH, NaOH, or alkali carbonates instead of KOH, was without improvement.

M. R. Thompson (28), after an exhaustive study of the cyanide plating baths of different metals, expected that it should be possible to deposit germanium from a mixed cyanide bath, but apparently germanium cyanide does not exist in the pure state. On boiling a potassium cyanide solution with GeO_2, however, some of the dioxide went into solution. Possibly, hydrolysis of potassium cyanide forms the hydroxide which dissolves the dioxide. Upon electrolyzing such a solution, no deposit of the metal was obtained. The addition of some alkali was necessary before the deposition could take place.

Deposition from alkali sulfide baths.—Because a commercially successful sulfide plating bath is used for the recovery of antimony (30), and germanium is similar to that metal in many ways, the electrodeposition from solutions of the germanium sulfide in alkalies, alkaline sulfides, and potassium cyanide was studied. The disulfide, GeS_2, one of the most stable compounds of germanium, is prepared very easily (29) by saturating an alkaline solution of the dioxide with H_2S and then precipitating the disulfide by strongly acidifying the solution. It is soluble in alkali and alkaline sulfide solutions.

Though the deposition could not be carried beyond a certain limit, it

takes place much more easily from a sulfide bath than from an oxide bath of germanium. A further advantage is that ordinary room temperatures can be used for obtaining a thin coat of the metal, though slightly higher temperatures (around 45°C.) are recommended. One of the formulas used was as follows: GeS_2, 20 g./l.; KOH, 40 g./l.; Na_2S, 12 g./l.; temperature, 30°C.; and current density (cathode), 2.5 amp./dm.^{2}

Deposition from acid plating baths.—Though it was to be expected that the germanium deposition from solutions containing higher hydrogen ion concentrations would be more difficult than from highly alkaline baths, the acid plating baths were investigated because of the possibility of introducing higher germanium ion concentrations into the solution, thereby counteracting the higher hydrogen ion concentrations and increasing the possibility of deposition of the metal ion on the cathode.

Germanium dioxide dissolves in water, to a certain extent, giving a solution of germanic acid, H_2GeO_3. The solubility can be increased by addition of mannitol and other sugars. Upon electrolyzing such a simple solution, only very thin deposits of germanium were obtained. The effect of sulfuric acid additions was studied, beginning with extremely small quantities, until finally a suspension of GeO_2 in concentrated sulfuric acid was electrolyzed. In all cases, there appeared to be no improvement of the deposit.

Electrolysis of germanium dioxide in potassium hydroxide solution immediately after neutralizing with sulfuric, hydrochloric, oxalic, tartaric, citric, sulfamic, acetic, lactic, formic, or phosphoric acid produced only a thin germanium plate on the cathode. Additions of LiCl, NH_4Cl, or $CaCl_2$ to the chloride bath were without any beneficial effect.

GeO_2 is very soluble in a mixture of oxalic acid and ammonium oxalate which forms the basis of one of the methods of extraction (15) from the ore. A detailed investigation of deposition from this solution was made with no success.

Very thin, bright, and shiny deposits of germanium were obtained from baths made by dissolving germanium dioxide in fluosilicic acid. In the range of 2 to 100 g./l. of the dioxide, attempts to build up thick plates were unsuccessful. High temperature, 80°C., was required and traces of clove oil appeared to be beneficial.

Both germanium dioxide and germanium metal by anodic dissolution were found to be insoluble in fluoboric acid, in attempts to prepare plating baths. The dioxide dissolved readily in hydrofluoric acid to form fluogermanic acid, but no deposition took place on the cathodes with or without addition compounds, such as: potassium, ammonium, hydrazine, aniline, and ethylenediamine fluogermanates.

Deposition from neutral solutions containing amines.—The solubility of germanium dioxide in water is increased by triethanolamine, apparently forming the soluble $[(C_2H_4OH)_3N]_nGe^{4+}$. Although other metals such as copper, cobalt, nickel, and tungsten have been electrodeposited from amine solutions, e.g., by Brockman and coworkers (31), such baths were not successful for germanium in the present work.

Effect of low temperatures and high current densities on deposition from aqueous solutions.—Most of these experiments on the deposition of the germanium metal from aqueous solutions were repeated using temperatures around 0°C. Lower temperatures were used if solutions did not start depositing out crystals.

The effect of raising the cathode current density was also studied at these lower temperatures. The maximum current densities used for a short time were of the order of 100 amp./dm.^{2} The deposition did not improve with any of these variations, and it was impossible to obtain a deposit that grew continuously, though the temperature was varied from freezing to boiling. It is, however, a noteworthy fact that the total deposition of the metal per unit surface of the cathode was greater from some solutions than from others.

Experiment with rotating cathode in aqueous solutions.—Other researches (32, 33) have shown profound effect on cathodic deposition of metals as a result of high speed rotation of the cathodes. Therefore, this technique was studied in the work on germanium. Copper disks, $1\frac{1}{4}$-inch diameter, were used as cathodes rotated at speeds up to 4000 r.p.m. Again only a thin plate of germanium was obtained. One improvement was noted. Where a temperature of at least 90°C. was required with the stationary cathode, the same thin deposit could be obtained at room temperature on the rotating cathode.

Anodic behavior of germanium in aqueous solutions.—In neutral salt solutions, germanium anodes were insoluble, and not attacked. In concentrated alkali or acid solutions, the metal is anodically oxidized. Under some conditions, such as high current density, some loss occurs through the formation of an oxide layer that peels away and dissolves in the bath. Anodic behavior seems unsuitable for plating baths.

Codeposition of germanium with copper and other metals.—Germanium forms a series of alloys with a large number of metals. Among the more important of these are copper, silver, gold, magnesium, aluminum, nickel, iron, and tin. None of these alloys has been plated out of aqueous solutions, except that of germanium with tin which Schwarz (26) obtained from a solution of potassium germanate to which tin oxalate had been added. He did not make any detailed study of the deposition.

Many of the germanium alloys have interesting properties, for example, the increased hardness and rolling quality obtained by alloying aluminum with germanium, and the enhanced corrosion resistance of copper when alloyed with germanium.

An observation made when the initial experiments on the electroplating of germanium were in progress revealed that the presence of copper ions in the solution caused a beautiful coating of the alloy. This alloy of copper and germanium has physical and chemical properties similar to those of pure germanium metal.

Once the prerequisites for the deposition of the copper alloy became clear, the effect of the addition of small quantities of various metals to the germanium bath was investigated before making an exhaustive study of the copper-germanium alloy plating.

Preliminary alloy plating studies.—A standard alkaline bath of germanium was prepared as follows, and the effect of additions of various metals as their salts was studied:

	g./l.
GeO_2	2.6
KOH	170.0

The results obtained are given in Table I.

According to Table I, it is clear that codeposition of germanium with copper, silver, cobalt, nickel, and tin is possible from alkaline solutions.

For studying the deposition of germanium with tin, Schwarz (26) added tin oxalate to the alkaline germanium bath.

Tin as oxalate	0.209 g.
GeO_2	0.1052 g.
Potassium oxalate	10 g.
KOH	25 g.
Water	150 cc.
Temperature	90°C.
Current density	2.3 amp./sq. dm.

Experiments with his bath showed that the conditions have to be very rigidly controlled for the codeposition. At a lower temperature (50°C.),

TABLE I. *Preliminary tests on metal additions*

Volume of electrolyte in all experiments was 30 cc.

Metal added in form of a soluble salt	Amount of metal added	Results
	grams	
Copper	0.0127	A white lustrous deposit obtained immediately at room temperature. Weight, 0.0168 g.
Zinc	0.0010	A very faint coat dissolving in dil. HCl proving deposit of zinc only.
Silver	0.023	A silvery coat gave test for germanium and silver.
Cobalt	0.0005	A bright coat, weight 0.0012 g.
Lead	0.0010	A greyish shiny deposit of lead.
Vanadium	0.0007	No deposit.
Tin	0.0005 and more	Steel grey shiny deposit shows test for Ge when the temperature is above 85°C.
Mercury	0.0030	No deposit.
Nickel		On using nickel anode a deposit containing nickel is obtained at temperature above 80°C.
Iron (ferrous)	0.002	A flash coat of iron was obtained.

only a very small quantity of germanium, just enough to give a test for the metal, is deposited with the tin. The rate of deposition at the higher temperature is very slow and of little practical value.

Copper alloys were selected for further study, because of the ease of codeposition and useful properties. R. Schwarz and Elstner (6) examined the system copper-germanium and found that up to 17 per cent germanium the alloys are golden yellow in color. The two metals form the compound Cu_3Ge which contains 27.6 per cent germanium and is silvery white with a bluish cast. These alloys are stable toward hydrochloric acid. Above 20 per cent germanium, the alloys are attacked by aqua regia only. Concentrated H_2SO_4 has practically no effect on them (34). It thus appears that the alloys of copper with more than 20 per cent germanium have better chemical resistance than either of the constituent metals, and their deposition should be of practical value.

Preliminary study of the codeposition of copper and germanium.—First the

effect of addition of copper to an alkaline germanium bath was studied and then the effect of the addition of germanium, as dioxide dissolved in alkali, to an alkaline copper plating bath. The copper solution was prepared by dissolving a known quantity of copper cyanide in potassium cyanide.

Very interesting results were obtained in this part of the investigation.

All the deposits had the same bright, shiny appearance. Table II shows a definite relation between the amount of copper added and the amount of deposit obtained. Even after varying the concentration of copper within reasonably wide limits, the identical proportional increase in weight of the deposit was obtained. For confirmation of this conclusion about the composition of the deposit, a chemical analysis was made.

TABLE II. *Copper-germanium alloy deposits*

Addition of copper to germanium bath

GeO_2	0.4200 g.
KOH	5.0 g.
Water	30 cc.
Temperature	25°C.
Current density	1.25 amp./dm².

Copper added (as cyanide)	Calculated weight of equivalent alloy of composition Cu_3Ge	Total weight of deposit obtained	Nature of deposit
grams	*grams*	*grams*	
0.0610	0.0835	0.0827	Silvery bright
0.1830	0.2507	0.2460	Silvery bright
0.1441	0.1974	0.2000	Silvery bright
0.2440	0.3340	0.3251	Silvery bright

In all cases, the composition of the deposit was Cu_3Ge within limits of experimental error. A representative analysis is given below:

Weight of the deposit dissolved	Amount of copper found	Cu	Ge
grams	*grams*	%	%
(1) 0.1646	0.1190	72.1	27.9
(2) 0.1281	0.0930	72.7	27.3

The compound Cu_3Ge contains 27.6 per cent germanium.

Effect of varying of different factors in the deposition of Cu_3Ge.—Stirring had no effect on the composition of the alloy. The plate obtained is smooth and free from striations on gentle stirring of the bath. Upon increasing the temperature, the composition of the alloy did not change, but the quality of the alloy was affected. Instead of the shiny, bright deposits, dull deposits were obtained at the higher temperature. Also, the deposits obtained at temperatures higher than 30°C. did not keep well, darkening after only a few days. The deposits obtained at room temperatures remained shiny and bright for the last three months in the laboratory atmosphere. The concentration of alkali had no effect on the deposition or the composition of the alloy. Very satisfactory deposits were obtained when

the concentration was 40 g./l. and 160 g./l. The current density can be varied within wide limits, but 2 to 3 amp./sq.dm. is recommended.

In order to find the limits of deposition of the compound Cu_3Ge, the bath of composition as shown in Table III was prepared for studying the effect of increasing the copper concentration.

Table III clearly shows that when the weight ratio of copper to germanium from the alkaline solution is increased above 10, pure copper is preferentially deposited. A range of alloys having varying compositions does not appear attainable from this bath. An explanation for this is offered below in the discussion of these experiments. Upon adding small quantities of copper to a bath containing a comparatively large quantity of germanium, the deposition of the compound Cu_3Ge takes place as long as copper is in the solution, after which only hydrogen is evolved on the cathode.

TABLE III. *Copper concentration limits for Cu_3Ge deposits*

GeO_2	0.046 g.
KOH	1 g.
Water	30 cc.
Temperature	25°C.
Current density	1.25 amp./sq.dm.

Copper cyanide added	Weight ratio in solution copper/germanium	Deposit
grams		
0.0	—	No deposit.
0.179	3.9	Cu_3Ge
0.358	7.8	Cu_3Ge
0.537	11.7	Deposit of copper—no germanium.

Experiments on the addition of germanium dioxide to alkaline copper cyanide solutions (Table IV) gave results similar to those of Table III.

According to results shown in Tables III and IV, when the copper concentration of the solution is not more than 10 grams of copper cyanide per liter, the deposition of the alloy Cu_3Ge takes place, providing the weight ratio of copper to germanium in the solution is less than 10. For a satisfactory deposition of the alloy these two conditions have to be fulfilled.

Final bath for Cu_3Ge deposition.—The following bath was selected as most suitable for the deposition of the alloy, Cu_3Ge:

GeO_2	3.0 g./l.
CuCN	7.0
KCN	4.0
KOH	40.0

After dissolving the components in water, the solution should be filtered. The bath has excellent keeping qualities. One bath has given excellent deposits for at least three months. At room temperature (25°C.) and at a current density of 2.0 amp./sq.dm., excellent deposits were obtained on copper, nickel, steel, and zinc cathodes, with 90 to 95 per cent current efficiency. An insoluble, hard carbon anode was used. The deposits were bright, smooth, and well adherent to all the basis metals.

Stationary and intermittent corrosion tests were made on the deposits of the alloy plated on copper. It has excellent corrosion resistant properties with respect to 10 per cent alkali solutions, 1:1 hydrochloric acid, and 10 per cent sulfuric acid.

DISCUSSION OF RESULTS OBTAINED ON THE DEPOSITION OF COPPER-GERMANIUM ALLOY

By the application of the phase rule and the Nernst theory for calculating the electrolytic potential of a metal in a solution of the metal ions, Reinders (35), as early as 1903, attempted to correlate the electrolytic potential of an alloy in a solution containing ions of the component metals. He found that, when the two metals form a definite chemical compound, the solution potential of the compound is a specific constant. The experimental results obtained by G. Tammann (36) on the abrupt changes that occur in the solution potential of alloys at or near simple atomic ratios of the constituent metals has proved the point beyond doubt. This solution potential (or if

TABLE IV. *Composition of the cyanide bath for Cu_3Ge deposits*

Copper cyanide (CuCn)	3.0 g.
KCN	3.0 g.
KOH	4.0 g.
Water	300 cc.

Amount of GeO_2 added	Weight ratio Cu/Ge in solution	Result
grams		
0.05	60.1	Pure copper deposit.
0.15	20.0	Pure copper deposit.
0.25	12.0	Pure copper deposit.
0.30	10.0	White Cu_3Ge deposit.
0.35	8.57	White Cu_3Ge deposit.

we examine the reverse phenomenon, the deposition potential) of the intermetallic compound depends on the concentration or activity of the ions of both the metals in the solution. The observation of this definite potential of the intermetallic compounds has been used as a test for their existence and Pushin (37) successfully predicted the existence of a comprehensive series of binary metallic compounds by this method.

An examination of our results in the light of above facts supplies us with an explanation of the preferential deposition of the compound Cu_3Ge from solution containing ions of both metals. The deposition potential of the compound should be a function of both the copper and the germanium ion concentrations in the solution. With the ion concentration held between certain limits (Table III), the deposition potential of the alloy must be less than that of either copper or germanium and, therefore, the deposition of the compound is facilitated. When the copper ion concentration is raised, the deposition potential from the solution of the pure metal copper is lowered so much below that of the compound Cu_3Ge that only pure copper is plated out and continues to plate out until the Cu ion concentration falls below the optimum, when the alloy, Cu_3Ge, alone deposits out. Further addi-

tions of germanium dioxide to the original bath do not increase the germanium ion concentration sufficiently to make the deposition potential of the metal fall below that of hydrogen from the same solution, and that is why it has not been possible so far to obtain a thick deposit of pure metallic germanium from aqueous solutions under any circumstance.

On this same basis, by holding the copper ion concentration constant and by additions of the germanium dioxide to the solution, it should be possible to lower the deposition potential of the alloy compound below that of copper, so that the compound Cu_3Ge is preferentially deposited.

II. Electrodeposition of Germanium from Non-aqueous Solvents

INTRODUCTION

Since hydrogen deposited in preference to the metal in aqueous solutions, it was expected that better results would be obtained from non-aqueous solvents in which the concentration of hydrogen is very small. A review of the literature on electrodeposition from non-aqueous solvents indicated that deposition from Grignard compounds as used by Mathers and coworkers (38, 39) in the deposition of aluminum and magnesium had promise.

Since the germanium halides are fairly soluble in a wide variety of organic compounds, halide baths were also considered. The fluoride and the chloride were eliminated because of their volatility, the difficulty in their preparation, and their affinity for moisture. The iodide is stable and is readily prepared by the action of concentrated hydroiodic acid on GeO_2.

The electrolysis of certain organo-metallic compounds of germanium has been studied. Tchakirian[41], upon electrolyzing germanochloroform, $GeHCl_3$, or chlorogermanous acid in 7*N* HCl, obtained, at the anode, red $Ge(OH)_2$, while the liquid at the cathode became poorer in germanium. This indicated the formation of $[Ge^{(+2)}Cl_3]$ ions at the anode, followed by hydrolysis to give germanous hydroxide. Upon increasing the hydrochloric acid concentration, the germanous ion was oxidized to germanic by the chlorine liberated at the anode.

When sodium triphenyl germanide was electrolyzed in a liquid ammonia solution by Laurence, Foster, and Hooper (42) they obtained three products: hexaphenyl digermane, triphenyl germane, and nitrogen. The nature of the anode material had considerable influence on the amount of nitrogen evolved.

No other references were found on the electrolysis of germanium compounds in nonaqueous solvents. The main difficulty of obtaining the metal from Grignard's reagent is that the metal forms a part of the anion in case of the germanium compounds. Most of these compounds of germanium are relatively stable, as compared to those of magnesium and aluminum, which makes them more difficult to decompose electrolytically.

EXPERIMENTAL

Electrolysis of Grignard's compounds.—A mixture of phenyl germanium iodides was prepared by the action of germanium tetraiodide on phenyl magnesium iodide according to the following reaction:

$$C_6H_5MgI + GeI_4 \rightarrow (C_6H_5)_x\,Ge\,I_y + {}_xMgI_2, \text{ where } x + Y = 4$$

On electrolysis of this germanium compound dissolved in dry benzene,

no deposit of any sort was obtained. It was observed that the conductivity of these solutions was extremely small, indicating very little ionization.

Electrolysis of germanium tetraiodide in organic solvents.—Germanium tetraiodide was prepared by the action of hydroiodic acid on germanium dioxide (43). The compound was purified by crystallization from chloroform. Germanium tetraiodide is soluble in a wide variety of solvents. Even water dissolves it, forming a clear solution which decomposes slowly on standing. However, the electrolysis of water solutions did not give any deposits of the metal.

Upon electrolysis of solutions of the iodide in eleven organic solvents, which were dried and distilled to remove any moisture present, the results obtained were as given in Table V. In each series of tests, the concentration of the iodide was varied from 1 g. to 20 g. per 100 cc. of the solution.

TABLE V. *Preliminary electrolysis of organic solutions of* GeI_4

GeI_4 dissolved in	Result of electrolysis
Absolute alcohol	Cathode deposit of GeI_4 and GeO_2.
Benzene	Deposit of GeI_4.
Dioxane	Deposit of GeI_4.
Furfuraldehyde	A black resinous coat.
Pyridine, aniline, dimethylaniline	A black resinous coat.
Triethanol amine	No deposit.
Ethylene diamine	No deposit.
Glacial acetic acid	Deposit of GeI_4 and GeO_2.
Glycerine above 100°C.	Deposit of germanium metal.
Ethylene glycol 100°C.	Deposit of germanium metal.
Diethylene glycol 100°C.	Deposit of germanium metal.

Good adherent deposits of metallic germanium can be obtained from solutions of the germanium tetraiodide in ethylene glycol, diethylene glycol, and glycerol. On comparing the results of deposition from these three solvents, the ethylene-glycol solution was the best of all as regards rate of deposition and character of the deposit. A more extended examination of this solution was, therefore, undertaken.

Deposition of thick coats of germanium from ethylene glycol solutions of the iodide.—The ethylene glycol used in these experiments was the ordinary technical variety, which was purified and, at the same time, rendered anhydrous by fractional distillation. The fraction boiling in the range 197° to 198°C. was selected.

A copper cathode and a germanium anode were used during most of the experiments. The use of other anodes was also examined. Results obtained are given in Table VI.

Properties and nature of the germanium deposits from ethylene glycol.—The deposits, although bright in the beginning, became steel grey as the deposition progressed. Deposits obtained at low current densities are brighter than those obtained at higher current densities. Heavy silvery white deposits were not obtained under any condition. The deposits are brittle like the cast metal, and this quality increases as the thickness of the deposit is increased. The adhesion of the deposits is better on copper than on nickel. The deposit is not attacked by hydrochloric acid (1:1), dilute

sulfuric acid or 10 per cent alkalies, and maintains the steel grey luster on atmospheric exposure.

TABLE VI

I. Composition of bath

Ethylene glycol ..... 50 cc. Cathode..... copper
GeI_4..... 0.5 g. Anode..... germanium

Cathode current density	Metal deposited	Cathode current efficiency
amp./sq. dm.	*g./sq. dm.*	%
0.625	0.0025	2.38
1.25	0.0038	1.8
2.5	0.0087	2.1
	Temperature 140° to 150°C.	
0.625	0.0125	12.0
2.5	0.0450	10.8
	Anode corrosion efficiency 154%	

II. Composition of bath

Ethylene glycol..... 50 cc. Cathode..... copper
GeI_4..... 2.5 g. Anode..... germanium

Cathode current density	Metal deposited	Cathode current efficiency
amp./sq. dm.	*g./sq. dm.*	%
0.625	0.0340	32.2
1.25	0.1000	48.0
2.5	0.125	47.0

III. Composition of bath

Ethylene glycol ..... 50 cc. Cathode..... copper
GeI_4..... 5 g. Anode..... germanium

	Temperature 140° to 150°C.	

Cathode current density	Metal deposited	Cathode current efficiency
amp./sq. dm.	*g./sq. dm.*	%
2.5	0.263	55
2.5	0.163	34
2.5	0.206	43.5
	Anode corrosion 130%	

DISCUSSION OF THE RESULTS OBTAINED FROM ETHYLENE GLYCOL SOLUTIONS

Deposition from solutions of polyhydroxy alcohols and the impossibility of the deposition from other organic solvents, in all of which the germanium iodide is soluble, show that the deposition is dependent on some other factor

than simple solubility. It may be that the polyhydroxy compound forms with the metallic iodide some complex compound, from which deposition takes place more easily. The very smooth, anodic corrosion of the germanium metal in these solutions (in all cases above 100%) shows that part of the germanium goes into solution in the divalent form. The di-iodide, which is not very soluble in organic solvents, is however retained in this solution.

Germanium tetraiodide concentration.—Because of the low metal content of the tetraiodide (Ge 12.5%), the metal ion concentration in the solution is comparatively low. The solubility of the iodide in glycol limits the increase of the concentration of the metal ion. Another important factor to be considered is the loss by sublimation of the iodide from the surface of the solution at the higher temperatures of operation. The results show an increase in the efficiencies with increase in the concentration of the iodide, as well as faster rates of deposition. Nevertheless, above a concentration of 5 g. of the iodide per 50 cc. of the solution, the loss due to vaporization of the iodide from surface overweighs these increased efficiencies. Plates obtained at lower concentrations are brighter.

Temperature.—At room temperatures, no deposits were obtained. The metal plates out only when the temperature is increased at least to 100°C. Higher temperatures give better plates as well as better deposition efficiencies. The voltage of operation also decreases as temperature is increased. Thus, in the bath containing 2.5 g./50 cc. of the iodide, the voltage dropped from 20 volts at 100°C. to 11 volts at 150°C. for a current density of 0.625 amp./sq.dm.

Current density.—With an increase of current density, the current efficiency of deposition increases. At the same time the brittleness of the plate is increased. The adhesion of the metal plate to the cathode surface depended on the current density used initially. The brightness of the plate is also a function of the current density, lower densities being more conducive to good deposits.

Anodes.—All the preliminary experiments were made with very pure carbon anodes, to avoid any metallic impurity vitiating the results. Platinum was also a satisfactory anode. The iodine liberated at an insoluble anode and the high temperatures of operation cause oxidation of the glycol. To avoid this difficulty, the anodic behavior of the pure germanium metal was studied. The metal is very smoothly corroded, and anodic efficiencies range from 130 to 150 per cent. This shows that part of the metal possibly goes into solution as divalent germanium. Better deposits were obtained when germanium was used as anode than when platinum was used as anode. To counteract the abnormal corrosion efficiencies of germanium while maintaining the metal ion concentration in the solution, the use of parallel connected anodes of germanium and platinum is indicated, with the help of which the requisite current only can be made to pass through the germanium anode and thereby keep the germanium concentration of the bath constant.

Maintenance of the ethylene glycol bath.—At the higher temperature of operation (150°C.), the loss of the solvent by vaporization is considerable, and fresh solvent has to be added from time to time. The electrolysis cell was kept covered during operation to minimize the vaporization loss of both the solvent and solute. Upon lowering the temperature of the bath, a

crystalline precipitate of the iodide combined with some complex compounds containing iodine was obtained, but it dissolves on reheating the bath.

The rate and quality of deposition from the bath were best when it was freshly prepared. On using germanium anodes, there was a slight increase of efficiency which, however, soon decreased, showing that there might be an optimum relationship between the concentration of the germanic and germanous ions as well as any complexes formed in the solution. A quantitative chemical study of the solution was found to be impossible because of the instability of the complexes formed.

III. The Electrowinning of Germanium from Fused Baths

The successful application of fused electrolytes for obtaining metals which ordinarily cannot be electrodeposited out of aqueous solutions prompted the study of this type of bath for winning germanium.

Germanium shows considerable similarity to tungsten as regards its deposition from aqueous solutions. Both metals can be obtained only as thin deposits that do not grow on further electrolysis from alkaline solutions. Excellent yields of tungsten were obtained from fused borate and phosphate baths, in which tungsten oxide was dissolved (44).

Very little work was found on the electrowinning of germanium from fused baths. Hall and Koenig, on electrolysis of germanium dioxide dissolved in a molten electrolyte of equimolecular mixture of sodium and potassium carbonates, obtained alloys of germanium with the platinum cathode they used (25). Dennis and Tressler (18) used a fused potassium fluogermanate, K_2GeF_6, as well as a fused cryolite bath in which the oxide was dissolved. On electrolysis, some pellets of the germanium metal were obtained at the cathode. Losses due to the volatalization of the GeO formed as an intermediate compound were considerable. No detailed investigation was reported.

The solubility of the oxide in various fused salts was studied for leads to a suitable bath for electrolysis. The results obtained are given in Table VII.

On electrolyzing the fused carbonate bath, it frothed continuously, liberating carbon dioxide, yet small crystals of germanium metal were found on the side and the bottom of the graphite crucible which was used as cathode. Unsatisfactory results were obtained from the fused carbonate bath in which the solubility is not very great and the losses are high.

The solubility of the germanium dioxide in borax bath *is very high*, so a detailed investigation of the fused borate bath was undertaken.

Apparatus used for fused electrolytes

The apparatus used in this investigation was very simple. The graphite crucible, which served as the container as well as the cathode, was prepared from a graphite electrode. The outside diameter of the crucible was 2 inches and the inside $1\frac{1}{2}$ inches. The depth was $1\frac{1}{2}$ inches. A nichrome resistor furnace was used to heat the crucible. Two deep holes were bored in the side of the crucible, one for making electrical contact, and the other for inserting a thermocouple. A graphite rod suspended in the melt served as the anode.

After melting a weighed quantity of borax, a requisite quantity of the germanium dioxide was added. After about 15 to 20 minutes a clear melt

was obtained. The anode was then inserted, the temperature was adjusted and electrolysis was started. During the experiment the crucible was covered with an asbestos lid, through which the anode was inserted.

TABLE VII. *Solubility of germanium in fused salts*

Bath	Temperature	GeO_2 added	Observation
grams	°C.	*grams*	
NaOH, 10	400	3.0	GeO_2 addition forms sodium germanate which is dissolved, partially, in ½ hour.
Na_2CO_3, 5 K_2CO_3, 7	800	3.0	GeO_2 addition liberated CO_2 in quantity with frothing. The losses of GeO_2 carried by the gas are great. The sodium germanate formed partially dissolved.
NaCl, 5 KCl, 5 LiCl, 3	800	3.0	The oxide settled down without dissolving.
$Na_2B_4O_7$, 10	800	3.0 to 5	A clear melt obtained.
$Na_2P_4O_7$, 10 $NaPO_3$, 5	1000	3.0	A clear melt obtained.

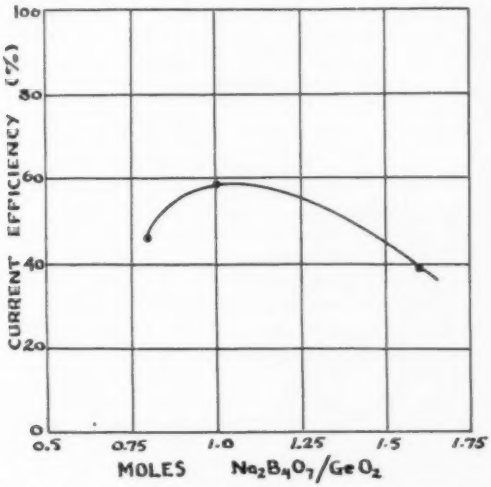


FIG. 1. Effect of mol ratio, borax/germanium dioxide, on current efficiency in the fused borate bath. Temperature, 1000° C. Cathode current density, 28.0 amp./sq. dm.

After the electrolysis was continued for the required time, the fused electrolyte at the top was poured into another graphite crucible. The germanium (m.p. 958°C.) which had collected at the bottom of the crucible in a molten condition was removed, cooled, freed from adhering electrolyte

by boiling in water, and weighed. In an experiment on a larger scale, it would be possible to tap the metal from the bottom of the crucible, since the specific gravity of pure fused borate is 2.5 and that of GeO_2 is 4.7, while the density of the solid metal is 5.3 (45).

DISCUSSION OF RESULTS OBTAINED WITH FUSED BORATE BATHS

The data for fused borate baths are shown graphically in Fig. 1, 2, 3, and 4.

Determinations of the purity of the electrowon germanium were made by dissolving the metal in fused alkali, precipitating the sulfide, and finally weighing the oxide formed by treating the sulfide with nitric acid. The metal was above 99.1 per cent pure in all of the determinations made.

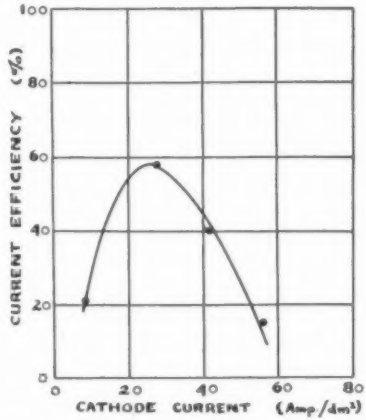


FIG. 2. Effect of current density on the current efficiency in fused borate bath. Temperature, 1000° C. Mol ratio, borax/germanium dioxide equaled 1.0.

Electrolysis of the phosphate bath as given in the solubility experiments was not so satisfactory as that of the borax bath.

It was found that: (a) as the mol ratio of borate to germanium dioxide was increased, the efficiency of deposition increased, up to a ratio of 1 and after that it decreased rapidly; (b) the current density had a decided influence upon the deposition, the optimum c.d. was 28 amp./sq.dm., the efficiencies were less on both sides of this value; (c) the current efficiency increased with increase in the temperature. Below 900°C. the efficiency is very low.

The conditions for the most efficient deposition of the metal were found to be:

Temperature	1000°C.
Mol ratio $Na_2B_4O_7$:GeO_2	1.0
Current density	28 amp./sq.dm.

The results, in general, bear out the sodium film theory proposed by Fink and Ma (44) in their studies on the electrodeposition of tungsten from

borate and phosphate baths. The increase in efficiencies of deposition above 900°C. is attributed to the formation of a sodium vapor film on the cathode surface. The boiling point of sodium is 878°C. The thickness of

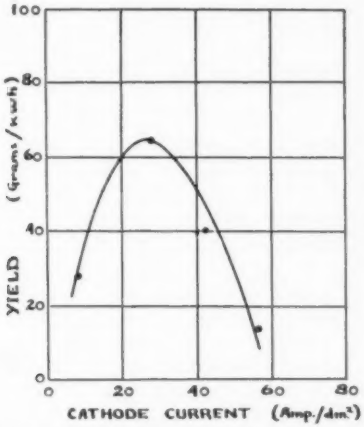


FIG. 3. Effect of current density on yield per kw.-hr. through the fused borate bath. Temperature, 1000° C. Mol ratio, borax/germanium dioxide equaled 1.0.

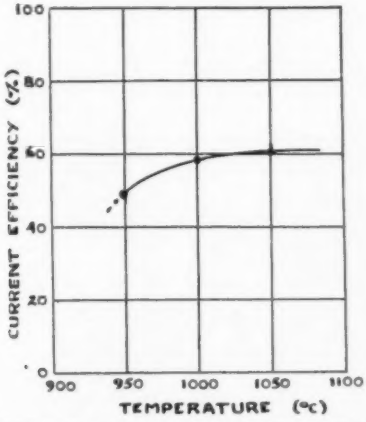


FIG. 4. Effect of temperature on current efficiency in the fused borate bath. Cathode current density, 28.0 amp./sq. dm. Mol ratio, borax/germanium dioxide equaled 1.0.

this film is also governed by the raio of sodium tetraborate and GeO_2 in the fused melt. In the deposition of germanium the film thickness is optimum when the mol ratio is unity.

The current density has a considerable effect on the sodium film. At

lower current densities, the yields were lower because the film thickness was less. The decrease in the efficiency and yields of germanium metal at higher current densities can be explained as follows: first, the sodium vapor film was too thick for a proper deposition of germanium metal; and second, local high temperatures produced at higher current densities helped in the vaporization of the monoxide, GeO, which was formed as an intermediate stage in the reduction of the dioxide.

The excellent deposition of germanium from borax baths can be explained by the high solubility of the dioxide, GeO_2, as well as that of the monoxide, GeO.

It is possible to operate the fused borax bath continuously by adding germanium dioxide to the melt and tapping out the molten germanium from the bottom of the cell. From time to time additions of fused borate and/or boric acid will have to be made to take care of any decomposition losses and to keep the ratio $Na_2B_4O_7/GeO_2$ constant.

SUMMARY

I. A continuously growing deposit of germanium metal was not obtained from any aqueous solution. After the cathode surface was covered with a thin film of the metal, further deposition stops and only hydrogen is evolved. Alkaline sulfide-baths were found to be superior to the oxide baths previously used to deposit thin films.

The codeposition of germanium with copper, tin, nickel, and cobalt from alkaline baths was studied. The most interesting alloy was the germanium-copper alloy, Cu_3Ge.

II. A bath consisting of a solution of germanium tetraiodide in ethylene glycol is satisfactory for obtaining thick deposits of the metal. The working temperature of this bath is between 140° and 150°C., and cathode current efficiencies as high as 48 per cent were obtained. The deposits were steel grey in color and fairly brittle. Germanium metal dissolved anodically with an efficiency above 130 per cent. This is the first time metallic deposits have been obtained from a glycol bath.

III. A new process for obtaining the germanium metal from its dioxide by electrolysis of the dioxide dissolved in a fused sodium tetraborate bath is described.

ACKNOWLEDGMENT

One of the authors (V. M. Dokras) wishes to express his thanks to the Government of Central Providence and Berar, India, for the award of a scholarship which enabled him to carry out the work at Columbia University, New York.

Any discussion of this paper will appear in the discussion section of Volume 95 of the TRANSACTIONS of the Society.

REFERENCES

1. CL. WINKLER, *J. prakt. Chem.* **34**, 208 (1886).
2. ROBT. SCHWARZ, *Z. angew. Chem.* **48**, 219 (1935).
3. U. C. TAINTON AND E. T. CLAYTON, *Trans. Electrochem. Soc.*, **57**, 279 (1930).
4. E. CORNELIUS, *Electronics*, **19**, 118 (1946).
5. PENDER MUELLER, U. S. Pat. 1,739,256, January 10, 1929.
6. ROBT. SCHWARZ AND GERT. ELSTNER, *Z. anorg. Chem.*, **217**, 289 (1934).
7. T. R. BRIGGS, R. O. MCDUFFIE, AND L. H. WILLISFORD, *J. Phys. Chem.*, **33**, 1080 (1929).
8. R. I. JAFFE, N. H. SMITH, AND B. W. GONSER, *Met. Tech.*, paper #1812, A.I.M.E., June, 1945.

9. W. J. Kroll, *Metall u. Erz.*, **23**, 682 (1926).
10. R. I. Jaffe, E. W. McMullen, and B. W. Gonser, *Trans. Electrochem. Soc.*, **89**, 277 (1946).
11. U. C. Tainton, *Trans. Electrochem. Soc.*, **63**, 153 (1933).
12. W. I. Patnode and R. W. Work, *Ind. Eng. Chem.*, **23**, 204 (1931).
13. L. M. Dennis and J. Papish, *J. Am. Chem. Soc.*, **43**, 2131 (1921).
14. M. S. Gable, *Rec. trav. chim.*, **52**, 225 (1927).
15. A. Tchakirian, *Compt. rend.*, **187**, 229 (1927).
16. L. M. Dennis, K. M. Tressler, and F. E. Hance, *J. Am. Chem. Soc.*, **45**, 2033 (1923),
17. NDRC Interim Report No. 1, Contract OE Msr 1408, Nov. 21, 1944 (National Research Council, Washington, D. C.)
18. L. M. Dennis and K. M. Tressler, *J. Phys. Chem.*, **31**, 1429 (1929).
19. OSRD Progress Report NWP-P 443K Contract OE. Msr 1139, Aug. 1, 1944 (National Research Council, Washington, D. C.)
20. E. Einecke, *Chem. Ztg.*, **61**, 989 (1937).
21. C. C. Bidwell, *Phys. Rev.*, **19**, 447 (1922).
22. Hodgeman, "Handbook of Chemistry and Physics," 25th Edition, p. 496, Chemical Rubber Publishing Co., Cleveland, Ohio (1941).
23. "Modern Electroplating," pp. 315-329, The Electrochemical Society, New York (1942).
24. *Ibid.*, 221.
25. J. Ivan Hall and Alfred E. Koenig, *Trans. Electrochem. Soc.*, **65**, 215 (1934).
26. Robt. Schwarz, *Z. anorg. Chem.*, **229**, 146 (1936).
27. Colin G. Fink and Frank L. Jones, *Trans. Electrochem. Soc.*, **59**, 461 (1931).
28. M. R. Thompson, *Trans. Electrochem. Soc.*, **79**, 417 (1941).
29. "Inorganic Synthesis," Vol. II., p. 104, McGraw-Hill Book Co., New York (1946).
30. D. M. Liddell, "Handbook of Non-Ferrous Metallurgy—Recovery of Metals," p. 130, McGraw-Hill Book Co., (1945).
31. Chas. J. Brockman and Coworkers, *Trans. Electrochem. Soc.* **69**, 535 (1936); **71**, 255 (1937); **73**, 352, 365, 371 (1938).
32. Colin, G. Fink, *J. Chem. Educ.*, **12**, 520 (1935).
33. Colin G. Fink and Henry B. Linford, *Trans. Electrochem. Soc.*, **72**, 461 (1937).
34. De Ment and Drake, "Rarer Metals," p. 68, Chem. Publishing Co., New York (1946).
35. W. Reinders, *Z. phys. Chem.*, **42**, 225 (1902).
36. G. Tammann, *Z. anorg. Chem.*, **107**, 139 (1919).
37. N. A. Pushin and P. N. Laschtschenko, *Z. anorg. Chem.*, **56**, 1 (1908); **62**, 34 (1909).
38. R. D. Blue and F. C. Mathers, *Trans. Electrochem. Soc.*, **69**, 519 (1936).
39. D. M. Overcash and F. C. Mathers, *ibid.*, **64**, 305 (1933).
40. Chas. A. Kraus and L. S. Foster, *J. Am. Chem. Soc.*, **49**, 462 (1927).
41. A. Tchakirian, *Compt. rend.*, **204**, 117 (1937).
42. L. S. Foster and G. S. Hooper, *J. Am. Chem. Soc.*, **57**, 76 (1935).
43. W. C. Fernelius, "Inorganic Synthesis," Vol. II, p. 112, McGraw-Hill Book Co., (1946).
44. Colin G. Fink and C. C. Ma, *Trans. Electrochem. Soc.*, **84**, 33 (1943).
45. "International Critical Tables," Vol. I., p. 153 McGraw-Hill Book Co., New York (1926).

THE RATE OF SOLUTION OF HIGHEST PURITY ALUMINUM IN SODIUM HYDROXIDE SOLUTIONS[1]

M. E. STRAUMANIS

School of Mines and Metallurgy, University of Missouri, Rolla, Missouri

AND

N. BRAKŠS

Chemical Laboratory, University of Latvia, Riga, Latvia

ABSTRACT

A series of dissolution experiments on highest purity aluminum (99.998%) in NaOH solutions ranging from 0.1 to 5*N* has been carried out. The rate of solution in parallel experiments shows deviations up to ±30 per cent from the average value. Homogenization attempts did not improve the results. The rate of solution in NaOH (up to 0.5 or 1*N*) is proportional to the cube root of the concentration of NaOH. In the region between approximately 0.5 and 3*N* the rate increases proportional to the concentration. Then follows a sudden jump and at concentrations above 4*N* the rate increases again, probably proportional to the concentration. At concentrations higher than 5*N*, the dissolution process is very irregular and deep pits are formed. Upon reducing the concentration below 5*N* NaOH (the Al plates were washed and the dissolution continued in fresh NaOH of lower concentration) the rate of solution drops only gradually, remaining considerably higher than when working with increasing NaOH concentrations. When the corroded surface was removed mechanically, the previous velocity could be observed within the limits of reproductibility.

INTRODUCTION

There are contradictions in previous publications on the dissolution of aluminum in bases: Jablczynski and Hermanoviez (1), as well as Centnerszwer and Zablocki (2), found a rate of solution proportional to the square root of the concentration of the base, while according to Bailey (3), a simple proportionality exists. Streicher (4) found that the weight loss of commercially pure aluminum is directly proportional to the hydroxyl ion concentration up to 0.3*N*, but between 0.1*N* and 0.5*N* the rate of dissolution is proportional to the square root of the hydroxyl ion concentration. The purpose of this paper is to show how the purest aluminum available (99.998%) reacts with sodium hydroxide over the entire range of concentration up to 5*N*, a problem which has not been investigated previously. The results of the work will help to resolve the contradictions mentioned above.

EXPERIMENTAL

The aluminum contained as impurities: Fe—0.0002%; Si—0.0009%; Cu—0.0003%; and others to give a total amount of 0.002 per cent (5).

[1] Manuscript received August 16, 1948. This paper, (which is an extract from a manuscript written at the University of Latvia in spring, 1944, but not published because of the war) prepared for delivery before the Philadelphia Meeting, May 4 to 7, 1949.

Samples were cut directly from the ingot and were 15.9 mm. in diameter and 4 mm. thick. The surface intended for the dissolution experiment was smoothed with a file and then polished with a polishing wheel and levigated aluminum oxide. After the other surfaces of the plates (see below) were protected, the polished surface was washed carefully with distilled water and then with alcohol and ether. All reagents used were chemically pure (Schering-Kahlbaum or Merck, pro anal. or puriss.).

An apparatus similar to that previously described (6), but technically improved, was used for the work. Measurement of the volume of evolved hydrogen was used to determine the velocity of metal dissolution. The dissolution of the samples was carried out in a 250 ml. double neck flask B

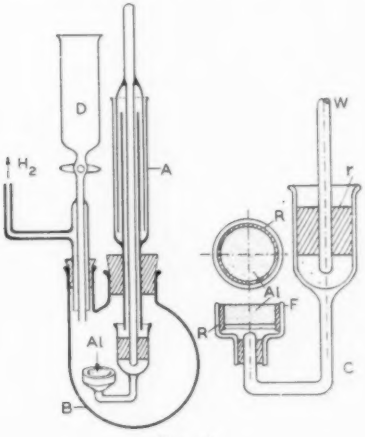


FIG. 1

Left. Apparatus for dissolution experiments. A. stirrer with Hg closure, B. flask, Al. plate with rubber insulation, D. filling funnel.
Right. Holder with plate. R. r. rubber insulation and stopper, F. plate holder, C. support basis, W. shaft of the stirrer.

(Fig. 1) of Jena glass. The evolved hydrogen was conducted into a gas burette by glass capillary tubes and vacuum tubing.

Experiments showed then that the usual materials, for example, wax, paraffin, etc., used for protection of the surfaces were unsatisfactory because the alkaline solutions penetrated into the gap between the metal and the insulation and the active surface increased to an unknown extent. This could be prevented with the help of rubber protection at least during the first hours of the experiment (Fig. 1, right). Impurities, such as glass powder or mercury falling out of the upper part of the stirrer (Fig. 1, left) remained in the upper enlargement of the base of the plate holder and did not fall into the solution.

In all experiments the position of the plate was at 45 degrees relative of the axis of the rotating shaft. All rubber parts contacting the solution were "prepared" by boiling them in solutions corresponding to those used

in the experiment, and rinsing with water. Two parallel runs were made in one thermostat at 25 ± 0.02°C. The velocity of stirring was about 120 ± 5 revolutions per minute. Each vessel for every experiment was filled with 200 ml. of the solution warmed to 26°C. When it cooled down to 25 degrees, the stopcocks were closed and the collection of hydrogen started.

TABLE I. *Rate of dissolution of 99.998% Al in 0.5 N NaOH, kept for 7 months in the glass flask, Fig. 1*

t	Experiment 1_a		Experiment 1_b	
	v_0	$\frac{\Delta v}{\Delta t F} 10^3$	v_0	$\frac{\Delta v}{\Delta t F} 10^3$
10	1.07	54.3	1.07	54.3
20	1.61	27.4	1.61	27.4
30	1.97	18.3	1.97	18.3
40	2.32	17.8	2.37	17.8
50	2.68	18.3	2.68	18.3
60	2.95	13.7	2.95	13.7
80	3.57	15.7	3.66	18.0
90	3.80	11.7	3.97	15.7
100	4.07	13.7	4.32	17.8
120	4.69	15.7	4.99	17.0
180	6.46	15.0	7.03	17.3
240	8.43	16.6	9.12	17.7
300	10.40	16.6	11.20	17.6
360	12.57	18.4	13.40	18.6
390	13.66	18.5	14.54	19.3
420	14.76	18.6	15.74	20.3
Average rate 60–360 minutes.....		16.3		17.7
1200	42.73	—	43.79	—
1260	45.13	20.2	46.28	21.0
1320	47.44	19.5	48.59	19.5
1500	54.60	21.8	55.84	21.8
1560	57.07	20.2	58.13	19.4
1620	59.15	17.6	60.21	17.6
1680	61.55	20.3	62.52	19.5
1740	63.67	17.8	64.64	17.9
1800	65.96	19.4	66.84	18.6
Average rate 1200–1800 minutes.....		19.6		19.5

DISCUSSION OF RESULTS

In spite of entirely similar manufacture of the Al plates, there were variations in the rate of the dissolution. This can be explained as resulting from an inhomogenous structure of the metal. The slight impurities in the metal block, in spite of all homogenization efforts, were not distributed uniformly. This non-homogenous distribution is the chief reason for the variations and fluctuations in the rate of dissolution in separate experiments.

Table I shows the progress of dissolution in 0.5N NaOH with the course

of time, while Table II illustrates the reproducibility of the experiments. In the tables, the following symbols are used:

t = time in minutes from the beginning of the experiment

v_0 = the volume of hydrogen read at the time t (accuracy 0.05–0.02 ml.), reduced to 0°C. and 760 mm.

F = the area of the soluble surface in cm.^{2}

$\frac{\Delta v}{\Delta t F} 10^3$ = the rate of dissolution, i.e., the amount of hydrogen in mm.^{3} evolved per cm.^{2} of the surface per minute between two readings.

The figures in Table I show that, at the beginning of the experiments, the plates dissolve more rapidly and more regularly than later. For one-half to one hour the reaction slows down slightly, the plates then dissolve at a comparatively constant rate for many hours, fluctuating only by few mm.^{3}/min. After 10–20 hours, the rate of the reaction increases and a very

TABLE II. *The average rate of dissolution of 99.998% Al in 0.5 N NaOH*

Time duration	$\frac{\Delta v}{\Delta t F} 10^3$ ave.
min.	
60–360	16.3
60–360	17.7
30–330	13.8
30–330	13.5
60–360	14.0
60–360	11 3
60–360	20.2
60–360	18.2
Average	15.6±4.6

flat maximum is formed between the 20th and 30th hour of reaction. More intense fluctuations are observed during this period.

After the experiments, the plates are glossy and no impurities can be observed. At a low magnification (Fig. 2) one observes shallow and deep etching cavities with smooth walls which have developed probably because of uneven distribution of the trace impurities in the aluminum.

As it is impossible to compare the entire course of all dissolution tests, the question arises as to which of the rates observed in the course of the experiments lasting more than 30 hours may be chosen for comparison. The results show that the reaction proceeds consistently enough for quite a long period, after the irregularities during the first one-half hour (dissolution of the highly deformed exterior layer of the metal). The first five-hour period, excluding the mentioned irregular starting period, was chosen in the experiments for comparison of the rates. This is justified as follows: (a) the velocity of dissolution reaches its maximum during the first hours of the reaction, since the higher rate in a later period is a result of the etching pits formed, (b) the area of the dissolving surface does not change considerably during the first hours (later the edge of the plate is eventually affected), (c) the procedure of dissolution is more regular at the

beginning than toward the end, (d) the experiments run were of shorter duration, and (e) the same plates, therefore, could be used for several experiments.

The average velocity of dissolution of duplicate aluminum plates, as determined by hydrogen evolution, lies between 11.3 and 20.2 mm.^{3}/cm.^{2} min. This variation is caused by the irregular distribution of the small amount of impurities still remaining in the aluminum. A better homogenization could not be obtained even by continued annealing.[2] Thus, a devi-

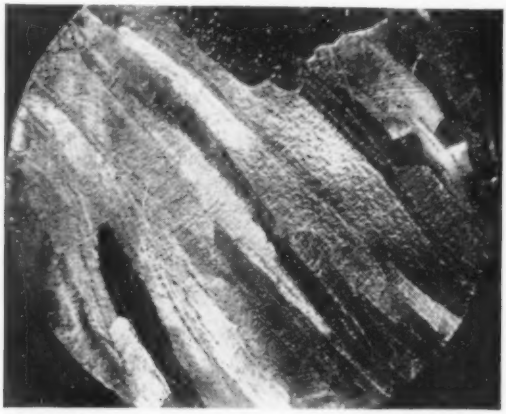


FIG. 2. Aluminum plate after dissolution in 0.5*N* NaOH. 5 ×.

TABLE III. *The dissolution of the 99.998% Al in 0.01 N NaOH.* D_a = 1.584 cm.; D_b = 1.590 cm., 25°C.

t	Experiment 9a		Experiment 9b	
	v_9	$\frac{\Delta v}{\Delta t F} 10^3$	v_9	$\frac{\Delta v}{\Delta t F} 10^3$
60–480	4.17	3.8	4.11	3.3
1320–1680	12.69	3.8	11.47	3.1
1680–1920	14.29	3.4	13.03	3.3
2700–2880	18.82	3.4	17.60	3.4
2940–3300	21.55	3.3	20.44	3.4
4320–4800	28.94	3.4	28.09	3.4

ation of 30 per cent from the average velocity must be taken into consideration. The other sources of error, however, play a subordinate role.

The velocity of dissolution of the purest Al in 0.01 to 5N NaOH.—Whenever possible, the same plates were used for all the runs, thereby attaining better reproducibility in the dissolution experiments. The use of dilute solutions generally insured longer service from the plates. The surface of each plate was treated before the beginning of every experiment as already described. The results of the dissolution experiments in 0.01N NaOH are shown in Table III. The plates dissolve in 0.01*N* NaOH with a very con-

[2] Some plates were annealed before the run in vacuum at 500° C. for 10 hours.

stant velocity over a period of 80 hours, although larger differences occur in short intervals. The process proceeds similarly in other dilute bases. Table IV shows the final results.

The increase in the rate of reaction with the concentration of the base is readily apparent. In more concentrated bases, the velocity becomes so rapid that, because of the formation of etching pits, the increased surface area becomes noticeable. It is, therefore, of no use to extend the tests over six hours.

At still higher concentrations of the base, unexpected results were found; on passing over to 4*N* NaOH, the rate of dissolution increases fourfold. Consequently, the experiments were carefully carried out and repeated many times with freshly made NaOH solutions of the purest materials (Merck and Kahlbaum) and several Al plates (10 runs). In all these experiments, the effect mentioned could be distinctly observed so that errors are excluded.[3] The hydrogen evolution is very irregular. The results of the dissolution experiments in 4 and 5*N* NaOH are listed in Table V. At still higher concentrations, the rate of dissolution was found to be so irreg-

TABLE IV. *The dissolution of the 99.998% Al in NaOH solutions of various concentrations at 25°C.*

t	N	$\frac{\Delta v}{\Delta t F}\ 10^3$ average
450–4680	0.02	4.4
600–1980	0.05	7.9
420–1800	0.1	9.4
480–1860	0.2	11.0
60–360	0.5	15.6
60–360	1.0	18.0
60–360	1.5	28.6
60–360	2.0	34.9
60–360	2.5	36.6
60–360	3.0	42.8

ular and the pitting, especially in the side of the plate, so deep that the use of more concentrated NaOH was of no value.

The aluminum surface after the runs appears dull and the boundaries of the grains are strongly marked. Magnification reveals droplike cavities covering the whole surface.

If the dissolution of such a plate is to be continued in more dilute solutions, no abrupt decrease in velocity of the reaction can be observed as is usually the case with dissolving metals. An aluminum plate that dissolves rapidly in 5*N* NaOH was washed and the dissolution continued in fresh 2.5*N* NaOH. The rate of solution was 3.5 times the rate previously observed (Table IV). If the corroded surface is removed by filing, polishing, etc., the previous velocity could be observed within the error limits. The prior exposure of aluminum to bases more concentrated than 4*N* gives it the property of dissolving 4 or 5 times more rapidly than when starting with more dilute bases (Fig. 3). It was impossible to determine whether this is produced by enlarging of the active surface by pitting or by other circumstances.

[3] The effect could not be observed in dissolution experiments of Al in KOH.

TABLE V. *Dissolution of the 99.998% Al in 4 and 5 N NaOH; volume of the solution 100 ml., 25°C.*

N	t	Experiment a		Experiment b	
		v_0	$\frac{\Delta v}{\Delta t F} 10^3$	v_0	$\frac{\Delta v}{\Delta t F} 10^3$
4.0	10	2.70	135	3.15	157
	20	5.76	153	5.85	135
	30	9.11	168	9.29	172
	60	19.98	181	20.70	190
	90	31.31	180	33.11	207
	120	43.19	198	46.43	222
	150	54.89	195	59.57	219
	180	66.86	200	73.24	228
	210	78.64	196	86.91	228
	240	90.60	199	100.94	234
	270	102.56	199	115.15	237
	300	114.61	201	127.54	240
Average 60–360			197.3		226.8*
4.0	60–360	97.73	163.0	106.0	176.7
5.0	60–210	59.65	201.8	59.25	201.2
5.0	30–330	113.77	189.6	112.18	187.2
5.0	60–180	41.10	171.3	47.7	199.0

* The plate shows deep lateral pittings. The figures, therefore, were not used below.

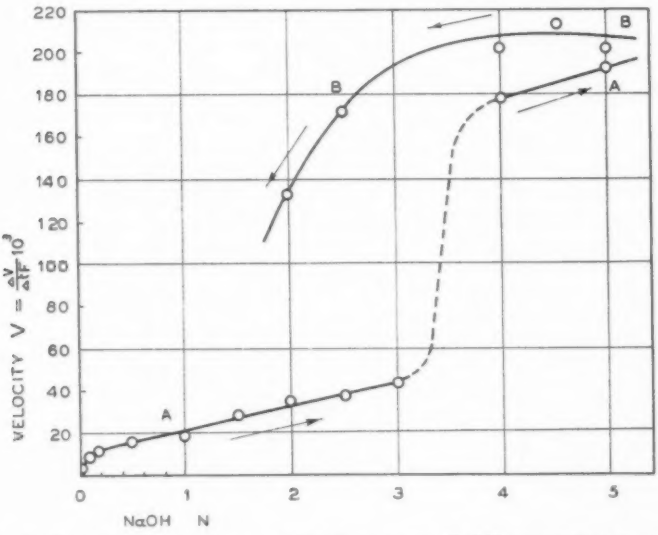


FIG. 3. Rate of solution of purest aluminum versus NaOH concentration. Curve A. increasing NaOH concentration, Curve B. decreasing NaOH concentration.

Table VI shows the influence of dilution of NaOH upon the velocity of dissolution.

As plotted in Fig. 3, Curve A can be divided into 3 parts: 1st part up to 1*N* NaOH, 2nd part from approximately 0.5*N* up to 3*N* (the curves over-

TABLE VI. *Rate of dissolution of 99.998% Al in 5 N NaOH, diluted by steps, 25°C.*

N	*t*	$\frac{\Delta v}{\Delta t F}\ 10^3$		Averages
		a	*b*	
5	60–210	201.8	201.2	202
4.5	230–280	214.4	211.3	213
4.0	310–350	223.0	205.2	204
4.0	360–410	191.5	191.5	
3.0	320–400	186.7	(234.0)*	194
3.0	370–400	205.7	189.2	
2.5	430–480	158.4	163.1	161
2.0	450–510	134.3	(188.4)*	134

* Not used because of deep pittings.

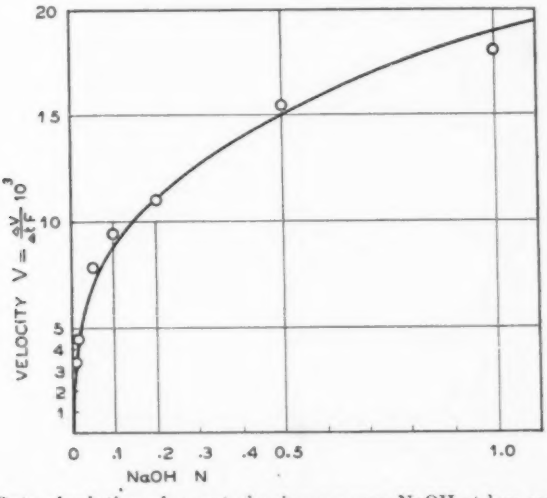


FIG. 4. Rate of solution of purest aluminum versus NaOH at low concentration. The curve follows the equation $V = 18.85\sqrt[3]{N}$.

lap), and the 3rd part over 4*N* NaOH. For clarity, the 1st part of the Curve A is shown on a larger scale in Fig. 4.

The rate of solution of purest aluminum in NaOH is proportional to the cube root of concentration (up to 1*N* NaOH);

$$V = 18.85\ \sqrt[3]{N} \qquad (1)$$

The first three points of the curve agree also with the square root statement of Jablczynski and Hermanovicz (1). At concentrations higher than approximately $0.4N$, the curve changes into a straight line, the empirical expression (correct from $0.5N$ up to $3N$) being:

$$V = 9.8 + 11N \qquad (2)$$

TABLE VII. *Comparison of the calculated and experimental dissolution rates* (V = *mm.*^{3}/*cm.*^{2} *min.*)*

N	V calc.	V found	Δ
0.01*	4.06	3.38	+0.68
0.02	5.12	4.4	+0.72
0.05	6.94	7.9	−0.96
0.1	8.75	9.4	−0.65
0.2	11.01	11.0	+0.01
0.5	14.92	15.6	−0.68
1.0	18.85	18.0	+0.85
0.2	11.03	11.0	+0.03
0.5*	15.3	15.6	−0.3
1.0	20.8	18.0	+2.8
1.5	26.3	28.6	−2.3
2.0	31.8	34.9	−3.1
2.5	37.3	36.6	+0.7
3.0	42.8	42.8	±0.0

* Equation (1) (see text) was used for normalities less than 1.0, and equation (2) was used for higher concentrations.

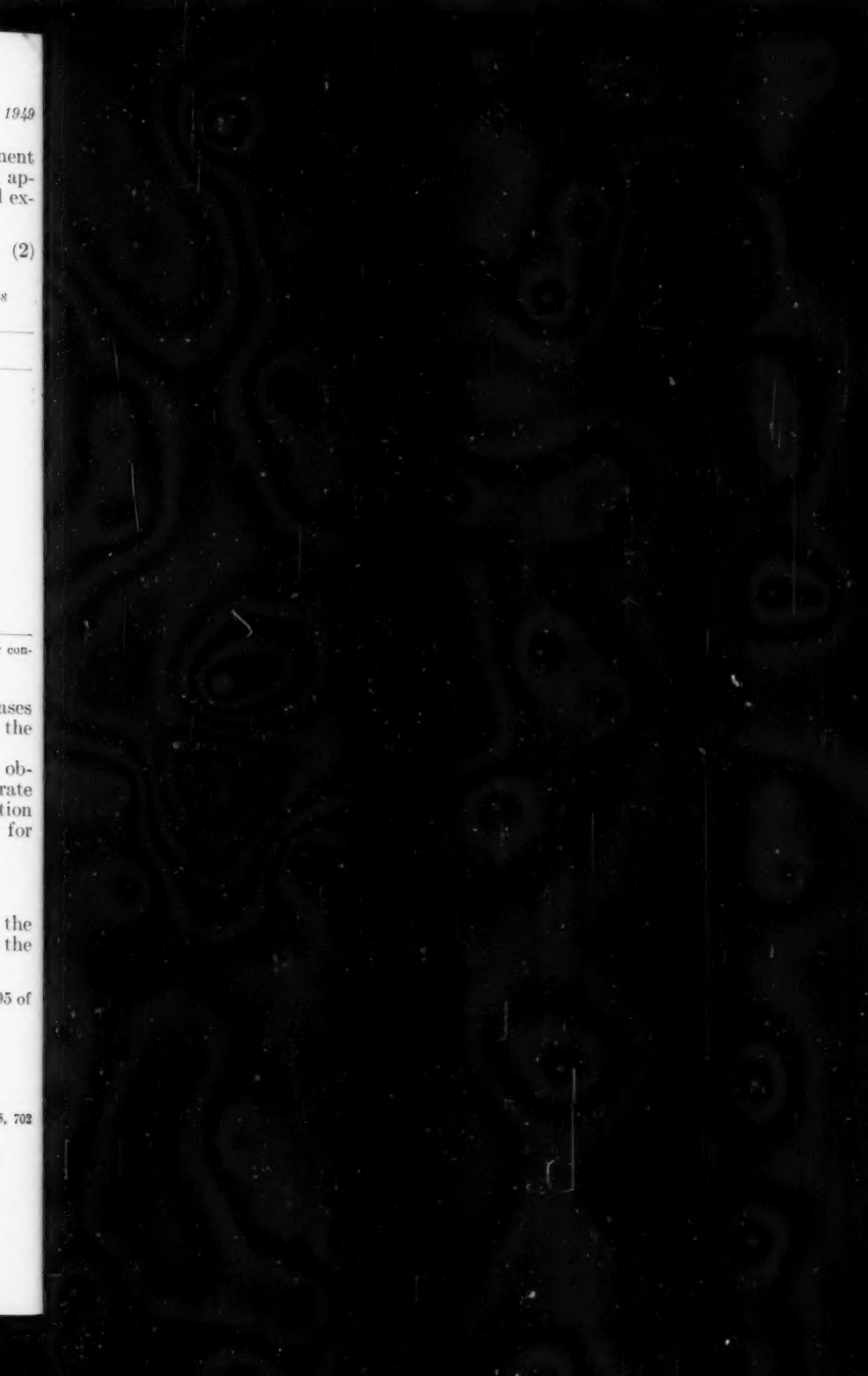
After a jump between 3 and $4N$ NaOH, the velocity of dissolution increases again, possibly proportional to the concentration. The accuracy of the two empirical formulas is shown in Table VII.

The tables and the curves show clearly why various investigators obtained different results in trying to find the relationship between the rate of dissolution and the concentration of the base, and present information concerning this relationship when aluminum of highest purity is used for the experiments.

ACKNOWLEDGMENT

We sincerely thank Professors A. W. Schlechten and A. Legsdin of the University of Missouri, School of Mines and Metallurgy for correcting the English of the present paper.

Any discussion of this paper will appear in the discussion section of Volume 95 of the TRANSACTIONS or the Society.

REFERENCES

1. K. JABLCZYNSKI AND E. HERMANOVICZ, *Roczniki Chem.*, **IV**, 466 (1926).
2. M. CENTNERSZWER AND W. ZABŁOCKI, *Z. physik. Chem.*, **122**, 455 (1926).
3. G. J. BAILEY, *J. Inst. Metals*, **9**, 79 (1912); *J. Soc. Chem. Ind.*, **39**, 118 (1920).
4. M. A. STREICHER, *J. Electrochem. Soc.*, **93**, 295, 297 (1948).
5. R. GADEAU, *Chimie & industrie*, **34**, 1021 (1934); *Ann. chim. anal.*, **19**, 64 (1937); *Metallwirtschaft*, **15**, 703 (1936); see also van Arkel, "Reine Metalle," p. 193, Berlin (1939).
6. M. STRAUMANIS AND N. BRAKŠS, *Korrosion u. Metallschutz*, **15**, 9 (1939).